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# HIGH RESOLUTION MILLIMETER-WAVE SPECTROSCOPY OF METAL 

 CONTAINING SPECIES: EXAMINING FUNDAMENTAL LIGAND INTERACTIONSby

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A Dissertation Submitted to the Faculty of the DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of DOCTOR OF PHILOSHOPHY

In the Graduate College
THE UNIVERSITY OF ARIZONA

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#### Abstract

Millimeter-wave spectroscopy has been used in this thesis to accomplish two main goals: 1) to study bonding, structural, and electronic properties of small, metalbearing molecules in their ground electronic states, in particular how individual metal atoms bond to small ligands, and 2) to provide rest frequencies for radio astronomical searches of metal containing species in the interstellar medium. The types of molecules studied in this thesis can be broadly classified into three groups: 1) alkali and alkalineearth amides $\left.\left(\mathrm{MNH}_{2}\right), 2\right)$ diatomic molecules in high electron spin or high orbital angular momentum electronic ground states (MX), and 3) transition metal cyanides (MCN). In this first category, the pure rotational spectra of $\operatorname{LiNH}_{2}\left(X^{1} \mathrm{~A}_{1}\right), \operatorname{LiND}_{2}\left(\mathrm{X}^{1} \mathrm{~A}_{1}\right), \mathrm{NaND}_{2}$ $\left(\mathrm{X}^{1} \mathrm{~A}_{1}\right), \mathrm{MgNH}_{2}\left(\mathrm{X}^{2} \mathrm{~A}_{1}\right)$, and $\mathrm{MgND}_{2}\left(\mathrm{X}^{2} \mathrm{~A}_{1}\right)$, were recorded and analyzed. For each, the first experimental monomer $r_{0}$ structures were determined. These species were found to be planar and not invert, in contrast to ammonia. In addition, for the alkaline-earth amides, the $\mathrm{M}-\mathrm{N}$ bond appears to become less ionic from Sr to Ca to Mg . The second class of molecules investigated, high-spin diatomics, includes: $\mathrm{NaC}\left(\mathrm{X}^{4} \Sigma\right), \mathrm{CrN}\left(\mathrm{X}^{4} \Sigma\right)$, $\operatorname{CrO}\left(X^{5} \Pi_{r}\right), \operatorname{MnF}\left(X^{7} \Sigma^{+}\right), \mathrm{FeN}\left(\mathrm{X}^{2} \Delta_{\mathrm{i}}\right), \mathrm{FeC}\left(\mathrm{X}^{3} \Delta_{\mathrm{i}}\right)$, and $\mathrm{TiF}\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$. These species represent examples of electronic states that have never or seldom been observed by high-resolution millimeter-wave spectroscopy, due to their high values of electron spin and orbital angular momenta. The analysis of their spectra has been used to test the adequacy of the effective Hamiltonians developed to model their rotational spectra; in particular the use of theoretically predicted higher order parameters. The final group studied includes the


transition metal cyanides $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{i}\right)$ and $\mathrm{NiCN}\left(\mathrm{X}^{2} \Delta_{i}\right)$. Unlike their alkali, alkalineearth, and group 13 counterparts, these species were determined to be linear cyanides with the metal atom bonded to carbon, similar to both $\mathrm{CuCN}\left(\mathrm{X}^{1} \Sigma^{+}\right)$and $\mathrm{ZnCN}\left(\mathrm{X}^{2} \Sigma^{+}\right)$. For both molecules, complications in the rotational spectra due to the Renner-Teller effect were observed and analyzed.

## CHAPTER 1. INTRODUCTION

Metal containing molecules are present in nearly every aspect of chemical research (Cotton et al. 1999). They are found at the center of large biomolecules such as proteins and enzymes (Moran et al. 1994), as catalysts in the production of olefins (Maldanis, Chien, and Rausch 2000), as potential high-density fuels (Brazier 1993), and even as organic synthesis reagents (Crabtree 1994; Gerald and Krause 1997). They are also important components of astronomical environments, for example, metal oxides and hydrides are used to classify star types (White and Wing 1978), and metal halides and cyanides have been detected in cold interstellar gas (Ziurys et al. 2002; Highberger and Ziurys 2003), suggesting a rich, yet unexplored chemistry. Therefore, their pervasiveness lends importance to the study of the structural, electronic, and bonding properties of these species, which can be accomplished by high-resolution spectroscopic techniques. In this thesis, millimeter-wave spectroscopy has been utilized to investigate small metal-bearing species via their pure rotational spectra.

Millimeter-wave spectroscopy is a high-resolution gas phase technique in which pure rotational transitions of a molecule, in its ground electronic state, are measured (Townes and Schawlow 1975; Gordy and Cook 1984; Carrington 1974). Using this method, many small metal-containing species (MC, $\mathrm{MN}, \mathrm{MCN}, \mathrm{MNC}, \mathrm{MNH}_{2}, \mathrm{MO}, \mathrm{MX}$, etc.) have been investigated (Sickafoose, Smith, and Morse 2002; Fougère et al. 2000; Merer 1989; Bernath 1997). Many of these molecules are radicals (unpaired electrons); they are short lived, usually difficult to synthesize, (requiring extreme reaction conditions) and produced in low quantity. The information obtained from the millimeter-
wave spectra of metal-bearing molecules has enabled structural and bonding trends to be established for many ligands. It has also provided computational chemists with an avenue to compare their results to experimental values, allowing them to improve calculation methods (see for example, Appendix D). In addition, these small molecules can serve as models for similar subsections in larger molecular systems. In such an environment, the interaction of the metal atom with a single ligand may not be easily probed and may be better understood by comparison to the isolated gas phase metalligand unit. Finally, many monomeric structures, i.e. methyl lithium, have only been obtained by gas-phase rotational spectroscopy (Allen et al. 1998).

The measurement of the pure rotational spectra of small metal containing molecules also provides an excellent method in which to test quantum mechanical theories of angular momentum. Since most of the species studied in the thesis are radicals, in particular the diatomics, the coupling of rotational, electron orbital and spin, and nuclear spin angular momenta must be considered (Townes and Schawlow 1975; Carrington 1974). These interactions present many complications in the analysis of the pure rotational spectrum of a molecule. In order to model these perturbations, specific quantum mechanical molecular rotational, fine, and hyperfine structure expressions have been developed (Brown et al. 1978). However, only in the last twenty years, with increased resolution and sensitivity in spectroscopic methods, have the predicted higher order perturbation components of these Hamiltonians been utilized (Hougen 1962; Brown and Milton 1976; Brown et al. 1981). These higher order terms were developed to describe molecules in very high electron spin and orbital angular momentum electronic
states, which until recently remained largely uninvestigated. In most cases, these terms were initially used in the fitting of optical/infrared electronic transition spectra; however, the highly convoluted nature of these spectra often limited their use. Application to higher resolution millimeter-wave studies has been severely limited due to lack of data. The study of metal containing molecules, which often have high angular momenta electronic states, by millimeter-wave spectroscopy, allows for these higher-order terms to be fully probed.

Finally, measurement of the millimeter-wave spectra of metal containing molecules provides a method to enable astronomical detection of these species in the interstellar medium (Rohlfs and Wilson 1996). In the cold environments of circumstellar gas, only the rotational energy levels of most molecules are populated. Radiative emission between these rotational levels is possible and can be collected using large sensitive radio telescopes. Astronomical observations at lab frequencies corresponding to the molecule of interest, accounting for the appropriate Doppler source shift, can be used to definitively detect a molecular species. This thesis however, concentrates on the measurement of the laboratory rest frequencies rather than the astronomical observations.

## CHAPTER 2. EXPERIMENTAL

1. Instrumentation
i. Low Temperature Spectrometer

The pure rotational spectra of the species studied in this thesis have been measured using the two direct absorption millimeter-wave spectrometers of the Ziurys lab (Ziurys et al. 1994). Figure 1 show a block diagram of the low-temperature instrument, in which those molecules containing alkali and alkaline-earth metals were studied. The spectrometer can be broken into four basic components, radiation source and phase-locking electronics, reaction chamber for molecular synthesis, detector and lock-in-amplifier, and data processing. Each of the sections, as well as the optics scheme, will be discussed in detail below.

## 1. Radiation Source

The millimeter-wave spectrometers of the Ziurys group are currently equipped to operate in the $65-650 \mathrm{GHz}$ frequency region of the electromagnetic spectrum, with near continuous coverage over this range. The radiation is produced by a series of Gunn diode oscillators (J. E. Carlstrom Co.) and Schottky diode multipliers (Millitech). Three Gunn oscillators provide radiation in the approximate ranges $65-95 \mathrm{GHz}$ (WR12), $90-120$ (WR10), and 102-136 (WR8). The Gunn oscillator consists of an InP diode, which is biased at approximately 10 V . Specific frequencies are obtained by adjusting the size of the oscillating cavity using two micrometers, a backshort and a tuning mic. Specification sheets with approximate micrometer settings are available for each Gunn and serve as the course frequency adjustment. The typical power output of the Gunn is less than 90 mW .


Figure 1. Block Diagram of the Low-Temperature Spectrometer.

The radiation propagates out of the Gunn into the appropriate sized waveguide, followed by an isolator, a magnetic device that serves to prevent reflections back into the Gunn oscillator. From there 10 dB or $10 \%$ of the radiation is coupled off into a harmonic mixer. If higher frequency radiation than the Gunn output is desired, Schottky diode multipliers (doubler, tripler, quadrupler, and quintupler) are utilized. The multiplier is typically biased at less than 10 V at a current of less than 10 mA . Two micrometers are available to maximize the output power of the multiplier, which typically ranges from less than 5 mW for the doubler to less than 1 mW for the quadruplers and quintupler. The
radiation is then launched from a corrugated scalar feed hom in one linear polarization in a Gaussian beam shape.

## 2. Phase Locking Electronics

The radiation coupled into the harmonic mixer is used to phase-lock the Gunn oscillator and to determine the radiation frequency to high precision. This is accomplished using a reference signal, provided by a $2 \mathrm{GHz}(1.8-2.2 \mathrm{GHz})$ synthesizer (Fluke 6082A). This 2 GHz signal passes through the triplexer, (a filter that allows 2 GHz to pass) and into the harmonic mixer. The mixer (Pacific Millimeter Products) generates all harmonics of 2 GHz up to $\sim$ the $80^{\text {th }}$, with varying efficiency. These harmonics are then mixed with the Gunn radiation. The 2 GHz synthesizer frequency is set to a value that when multiplied by a chosen harmonic is 100 MHz lower in frequency than the fundamental frequency of the Gunn, i.e. $v_{G u n n}-100 \mathrm{MHz}=v_{\text {Mult }} \times H A R M$. If the Gunn is properly tuned via the course adjustments, then a 100 MHz intermediate frequency (IF) will be produced by the addition of the Gunn and 2 GHz signal. This IF signal can pass through the triplexer, to a phase-lock box (XL Microwave 800/800A) and spectrum analyzer (HP 8595A/ Advantest R4131D). The correctness of the IF can be confirmed by changing the 2 GHz synthesizer frequency to correspond to a harmonic 1 to 2 units lower or higher. The IF is then compared to a standard 100 MHz reference oscillator (MTEQ) via the Gunn phase-lock box. If the phase of the IF matches the reference oscillator, the exact frequency of the Gunn is known and system is said to be phase locked. Scanning of frequency ranges is achieved by stepping the 2 GHz synthesizer. As this frequency changes, the phase lock box changes the bias voltage
applied to the Gunn oscillator in order to maintain phase lock. This fine adjustment is applicable for scanning ranges up to $\pm 100 \mathrm{MHz}$ of the fundamental frequency or for example, 400 MHz when using the quadrupler. Beyond this the Gunn must be manually retuned and the lock process repeated.

## 3. Optics Scheme

The spectrometer utilizes a Gaussian beam optics scheme in order to minimize radiation loss through the system. Teflon lenses are used as focusing elements and their placement is shown in Figure 2. Upon exiting the scalar feedhorn, H, the radiation is focused using a frequency dependent lens, L1. The beam comes to a waist at the polarizing grid (gold-coated tungsten wire), which ensures only the one linear polarization exiting the feedhorn passes. The front and rear of the reaction chamber are capped with Teflon lenses, L2 and L3, and are used over the entire frequency range of the spectrometer. After passing through L2, the radiation is refocused to a waist at the center of the reaction cell. It then exits the rear of the chamber through lens L 3 , where it strikes a rooftop reflector, $R$, reflecting the radiation back through the system with a $90^{\circ}$ polarization change. The radiation makes a second pass through the reaction chamber and exits towards the polarizing grid. The grid now acts as a mirror and directs the millimeter-waves into the detector, B , an InSb bolometer. A final frequency independent lens LA , collimates the beam into the light cone of the detector.


Figure 2. Optics Scheme for the Low-Temperature Spectrometer.

## 4. Reaction Chamber

The molecules investigated in this thesis were synthesized continuously, in the gas phase, at low pressure. The reaction cell is a 0.5 m long and 0.1 m diameter steel cylinder vacuum chamber, capped at the front and back by virgin Teflon lenses and contains several port openings for apparati essential to synthesis. The cell is continuously pumped by a mechanical/roots blower type pump (Edwards 1M40/2M40). Typical system pressures, without reactant gasses, range from $10-30$ mtorr. The reaction chamber contains a Broida type oven, shown in Figure 3, which serves as the source for metal vapor. Approximately, 1 mtorr of gaseous metal is produced by resistively heating a solid sample in an alumina crucible ( $\mathbb{R}$. D. Mathis C6-AO) in a tungsten wire basket, ( $\mathbb{R}$. D. Mathis B11-3x.040W), which is connected at each end to $1 / 4$ in diameter steel post. These posts are clamped into copper electrodes, which in tum are connected extemally,
via ceramic feedthroughs, to an ac power supply. In the center of the oven a $1 / 4$ in diameter tube extends $\sim 7$ in. below the bottom of the oven and is connected to the


Figure 3. Broida-type Oven.
oven jacket, which surrounds the tungsten basket. This tube allows for reactant gasses to enter the chamber. Reactant gas can also be added, through a tube, above the oven. A d.c. discharge electrode is located perpendicular to the top of the oven, approximately 2
in. above. The discharge electrode consists of a 0.25 in. diameter copper rod, 3 in. in length, connected externally to a d.c. power supply (Universal Voltronics BRC 10,000). Additional wires, copper or silver, can be attached to the end of the electrode as either one to three prongs or as a ring. The d.c. discharge electrode is grounded through the external portion of one of the copper oven electrodes, in order to direct the discharge through the metal vapor and create a plasma. A quartz window, 2 in . in diameter is located approximately 8 in . above the oven. From this viewpoint, the solid metal in the oven can be monitored along with any atomic emission or chemilumescence from the discharge plasma. Brightly colored plasmas are often observed with the alkali and alkaline-earth metals and are often a good indication of metal vapor production.

## 5. Detector and Lock-In-Amplifier

The detector is an InSb 'hot electron' bolometer (Cochise Instruments) cooled to $\sim 4 \mathrm{~K}$. The detector is cooled by means of a two-stage dewar, surrounded by a vacuum chamber ( $<1$ mtorr). The outer dewar contains liquid nitrogen, while the inner contains liquid helium. Before filling, the inner and outer dewars are pre-chilled with liquid nitrogen for $\sim 1$ hour. Liquid nitrogen is then reintroduced into the outer dewar, followed by liquid helium in the inner dewar (full is usually indicated by a pluming effect). Optimal cryogenic hold times are approximately 36 hours for the helium if the nitrogen is replaced every 12 hours. The detector employs a low noise preamplifier before sending the signal to a lock-in-amplifier. The radiation is frequency modulated (through the 2 GHz synthesizer) at ( $3 \mathrm{kHz} \times$ harmonic) at a rate of $\pm 25 \mathrm{kHz}$. The lock-in amplifier is set to detect signals from the detector, modulated at two times this rate, with the phase of
the incoming signal offset by $180^{\circ}$. Therefore, absorption signals have the appearance of a second derivative, Gaussian line shape, in emission.

## 6. Data Processing

The entire spectrometer operates under computer control via an IEEE-488 bus. The scanning software, SCAN20, was written by A. J. Apponi and operates in MS-DOS mode. Spectroscopic data is generally collected in two stages. First, searches for new molecules involve large frequency space survey scans, each in 100 MHz intervals. Second, final frequency measurements of absorption features are determined by using a minimum of one scan pair consisting of one scan in increasing and one in decreasing frequency, $5-7 \mathrm{MHz}$ in width. The center frequency of the line can be determined by fitting a Gaussian curve to the line shape. Additional scan pairs and general signal averaging in both stages may be necessary in order to observe weak signals.
ii. High Temperature Spectrometer

The high temperature spectrometer was used in this thesis to study all molecules containing a transition metal (Allen 1997; Apponi 1997). The design of the second instrument is slightly modified from the low temperature spectrometer. The phase locking electronics and detection scheme are identical between the two instruments, however, there are several differences involving the optics scheme and reaction cell. Also, the data collection software now used is WinScan, written by A. J. Apponi, and is Windows based. A block diagram of the instrument is shown in Figure 4.

## 1. Optics

In this instrument, the Teflon lenses have been removed, except for those located in front of the feed hom, L1, and the detector, L2. In their place, offset ellipsoidal mirrors were utilized, labeled as reflectors 1 and 2 . The front spectrometer lens was replaced with a polystyrene plug, covered in front and back with virgin Teflon film (0.007in. thick). The rooftop reflector, located at the rear of the reaction chamber,


Figure 4. Block Diagram of the High-Temperature Spectrometer.
also serves as the vacuum seal. A path length modulator is located in the center of the optics path for baseline smoothing and consists of two rooftop reflectors, one stationary
and the other movable, with adjustable speed and displacement settings. End point data, which corresponds to the absence of this device, are ignored and retaken.

## 2. Reaction Chamber

The reaction chamber for this instrument is a double walled, water cooled, steel cell ( $-27 \times 9 \times 9$ in.). The larger dimensions of the cell allow for three Broida-oven ports as shown in Figure 4. In this thesis work, only one oven was employed at a time, in the position closest to the rooftop reflector. Attempts at using a second oven, in the middle location, resulted in no noticeable increase in molecular production and deformed the front polystyrene plug. For the oven port used, the location of the dc discharge electrode and quartz viewing window are the same as in the low-temp instrument, however, the oven design differs. Modifications to the oven were employed to vaporize transition metals. Because of the excessive heat, the external copper electrodes were cooled by water jackets designed to slip over the electrodes, beneath the feedthroughs. The oven posts were constructed of Hastalloy (higher melting point steel alloy) and a smaller sized tungsten basket (R. D. Mathis B10-3x.040W) and alumina crucible (R. D. Mathis C5-AO) were used to further concentrate the heat. Pieces of zirconium felt (Zircar) were wrapped around the basket and the space between the basket and the oven jacket was filled with ceramic balls and pieces of alumina for insulation. For titanium, molybdenum posts (higher melting point than Hastalloy) and BN (R. D. Mathis C5-BN) crucibles (liquid titanium reacted with alumina) were found necessary. The oven power supply(R. D. Mathis LV750) provided up to $1500-1700 \mathrm{~W}$ of power. Typical system
pressures without reactant gases ranged from 20-40 mtorr due to the larger pumping system (Edwards E1M175/E2M175).
2. Synthesis

Table 1 contains a comprehensive list of the optimal synthetic methods employed for each of the metal species investigated in this research. Specific isotopes are listed if not observed in natural abundance.

Table 1. Synthetic Methods for Metal Containing Molecules.

| Mol. | RGas | Amt ${ }^{\text {a }}$ | C.Gas | Amt ${ }^{\text {a }}$ | Gas Inlet ${ }^{\text {b) }}$ | Discharge | Emiss. | Notes |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| NaC | $\mathrm{CH}_{4}$ | 20-30 | Ar | 10-15 | Bot/Bot | $0.5-0.7 \mathrm{~A} / 200 \mathrm{~V}$ | orange |  |
| FeC | $\mathrm{CH}_{4}$ | 10-15 | Ar | 20 | Bot/Bot | 0.7-1.0A/200V | -- |  |
| COCN | $(\mathrm{CN})_{2}$ | 15-20 | -- | --- | TOP | -me | --- |  |
| $\mathrm{Co}^{13} \mathrm{CN}$ | $\mathrm{H}^{13} \mathrm{CN}$ | 10-15 | -- | --- | Top | $0.2 \mathrm{~A} / 200 \mathrm{~V}$ | --- | $\mathrm{H}^{13} \mathrm{CN}$ <br> synthesized |
| NiCN | $(\mathrm{CN})_{2}$ | 3-5 | --- | - - | Bot | -- | - |  |
| CrN | $\mathrm{NH}_{3}$ | 10-15 | Ar | 10-15 | Bot/Bot | 0.7A | -- | $\mathrm{w} / \mathrm{N}_{2}$ weaker |
| FeN | $\mathrm{N}_{2}$ | 15-20 | --- | --- | Bot | 0.7-1.0A/200V | - | $\mathrm{w} / \mathrm{NH}_{3}$ weaker |
| $\mathrm{LiNH}_{2}$ | $\mathrm{NH}_{3}$ | 10 | Ar | 10 | Top/Top | $\cdots$ | -- |  |
| $\mathrm{LiND}_{2}$ | $\mathrm{ND}_{3}$ | 10 | Ar | 10 | Top/Top | -- | -- |  |
| $\mathrm{NaND}_{2}$ | $\mathrm{ND}_{3}$ | <10 | Ar | 30 | Bot/Bot | 0.04A/200V | orange |  |
| $\mathrm{MgNH}_{2}$ | $\mathrm{NH}_{3}$ | 10 | Ar | 10-15 | Top/Bot | $0.65-0.8 \mathrm{~A} / 30 \mathrm{~V}$ | green | oven lid |
| $\mathrm{MgND}_{2}$ | $\mathrm{ND}_{3}$ | 6 | Ar | 10-15 | Top/Bot | $0.65-0.8 \mathrm{~A} / 30 \mathrm{~V}$ | green | oven lid |
| CrO | $\mathrm{N}_{2} \mathrm{O}$ | 10-15 | Ar | 10-15 | Bot | 0.01 A 200 V | --- | no disch. required |
| TiF | $\mathrm{SF}_{6}$ | 3-5 | -- | --- | Bot | - | --- | BN crucible |
| MnF | $\mathrm{SF}_{6}$ | 20 | $\cdots$ | --- | Bot | - | - | w/ $\mathrm{F}_{2}$ also |

a) In mtorr.
b) Gas Inlet Location/Location refers to reactant gas first, carrier gas second.

In general, metal samples were obtained as $99 \%$ pure Aldrich products. For several of the metals, other sources, i.e. iron from steel rods, were found to be adequate. Several preparatory methods were found to be useful in improving the quantity of metal vapor produced and are listed in Table 2.

Table 2. Metal Preparations.

| Metal | Method |
| :---: | :---: |
| Lithium | source: Lithium ingot, cut pieces with tin snips melting; large bucket, must use stainless steel liner to prevent reaction with alumina; accumulates in oven bottom and often clogs gas inlet tube |
| Sodium | source: make sure to clean oil off cubes with hexanes first (do not order as small pieces) <br> melting: accumulates in oven bottom and often clogs gas inlet tube <br> cleaning; open several spectrometer ports, remove oven and place a large bucket with $\sim 2 \mathrm{in}$. of water under oven opening, slowly react sodium away by squirting, at a considerable distance ( $\sim 5$ feet), with water, connect top port to vent, cover laser table with plastic, do not remove front lens, this isn't as dangerous as cleaning potassium |
| Potassium | run away from this metal |
| Magnesium | source: turnings seem to work best subliming: warming oven slowly to sublimation point appears to produce a more consistent amount of vapor; on low-temperature instrument beware of coating rear lens; a green discharge is not a perfect indicator of magnesium reactivity; new magnesium works best |
| Calcium | source: storage of calcium, in any form, after first use in the dessicator will prolong lifetime |
| Iron | source: $1^{1 / 4-1} 1 / 2 \mathrm{in}$. length, $3 / 8 \mathrm{in}$. diameter cold rolled steel; clean first with hexanes, then sandpaper |
| Cobalt | source: grinding of outer surface of cobalt pieces (chips) with Dremmel tool decreases CoO melting: do not overpack chips in crucible |
| Nickel | melting: do not pack more than $3-4$ spheres(if starting material is in sphere form) in crucible at once to prevent falling together and not melting |
| Titanium | source: $11 / 4-11 / 2 \mathrm{in}$. length, $1 / 2 \mathrm{in}$. diameter titanium rod(TA CAID); file outside melting: cut 3-2 in. square pieces of zirconia felt with a hole slightly smaller in diameter than crucible; fit over crucible and basket to prevent Ti splashing onto basket |
| Manganese | subliming large basket is usable <br> reactions: seems to require a large amount of reactant gas |
| Vanadium | melting: alumina crucibles melt below Vanadium; reacts with BN |

## CHAPTER 3. GENERAL THEORY

1. Rotational Motion in a Diatomic Molecule

In quantum mechanics, the state of a molecule can be described by a complex function, known as a wavefunction (Levine 1991). The total wavefunction of a molecule can be broken down into components i.e. $\Psi_{\text {Tot }}=\Psi_{\text {Electronic }} \Psi_{\text {Vibrational }} \Psi_{\text {Rotational }} \Psi_{\text {Nuclear }} \ldots$, via the Born-Oppenheimer approximation (Levine 1991). Thus, the individual electronic, vibrational, rotational, and nuclear wavefunctions can be considered separately. The rotational wavefunction can be used to describe the end-over-end rotation of the nuclei. If the simplest molecule, a diatomic, is considered then to a first approximation it can be represented as a rigid rotor, consisting of two point masses connected by a rigid massless bar (Townes and Schawlow 1975; Gordy and Cook 1984; Carrington 1974; Bernath 1995). In this case, the rotational Hamiltonian can be written as,

$$
\begin{equation*}
\hat{\mathrm{H}}_{\mathrm{Rot}}=\frac{\hat{\mathrm{R}}^{2}}{2 \mathrm{I}} \tag{3.1}
\end{equation*}
$$

where $R$ is the rotational angular momentum, and I is the moment of inertia. The moment of inertia is directly related to the structure of the molecule, $I=\mu r^{2}$, where $\mu$ is the reduced mass of the molecule and r is the separation between the atoms. Using the time independent Schroedinger equation, the energies of the rotational levels can be obtained from Eq. (3.1), if one assumes a spherical harmonic form of the rotational wavefunction. The result is discrete rotational energy levels of the form

$$
\begin{equation*}
F(J)=E_{R O t}=B J(J+1) \tag{3.2}
\end{equation*}
$$

where $B=h / 8 \pi^{2} I(H z)$ is the rotational constant. Immediately, it can be seen that if $B$ can be determined, then the structure of the molecule can be known.

The $B$ value of a molecule can be measured experimentally by recording transitions between the rotational energy levels using the appropriate frequency of radiation. For a closed shell diatomic molecule without nuclear spin, Eq. (3.2) can be used to construct a rotational energy level diagram, as shown in Figure 5. In order for a transition to occur, the molecule must have a permanent electric dipole moment. The selection rule derived for electric dipole transitions is $\Delta J=+1$ (in absorption), and the allowed transition frequencies are given by the expression $v=2 B(J+1)$. If multiple rotational transitions are recorded, then these frequencies can be used to determine the rotational constant via a least squares fitting routine.


Figure 5. Rotational Energy Level Diagram for a Closed Shell Spinless Diatomic.

A diatomic molecule can not be expected, however, to remain completely rigid as it rotates. As the rotational angular momentum increases (higher J), the bond length of the molecule is expected to elongate slightly, as a result of centrifugal forces. This effect is accounted for by an expansion of the rotational energy level expression (Bernath 1995):

$$
\begin{equation*}
E_{R o t}=\mathrm{BJ}(J+1)-\mathrm{D}[J(J+1)]^{2}+\mathrm{H}[J(J+1)]^{3}+\mathrm{L}[J(J+1)]^{4}+\mathrm{M}[J(J+1)]^{5}+\ldots \tag{3.3}
\end{equation*}
$$

where $D, H, L$, and $M$ are the centrifugal distortion constants. Usually, only the first order distortion constant, $D$, is encountered.

The value of the rotational constant depends on the electronic and vibrational state of the molecule. In general, the pure rotational spectrum of a molecule is recorded in its ground electronic and vibrational states. However, if the molecules are not cooled significantly, there may exist some population in the excited vibrational levels and rotational transitions within these states may be observed. In a diatomic molecule, the vibrational motion consists solely of a stretch. Thus, the rotational constant is expected to decrease as $v$ (vibrational quantum number) increases, since $B \propto 1 / r$. The rotational constant of each vibration level can be expressed as $B_{v}$, and its vibrational dependence can be modeled by the following expression (Townes and Schawlow 1975):

$$
\begin{equation*}
B_{v}=B_{c}-\alpha_{e}(v+1 / 2)+\gamma_{e}(v+1 / 2)^{2}+\ldots \tag{3.4}
\end{equation*}
$$

where $B_{e}$ is the equilibrium rotational constant and $\alpha_{e}$ and $\gamma_{e}$ are rotation-vibration expansion constants. From $B_{e}$ the equilibrium bond length can be determined.

## 2. Perturbations to the Rotational Energy Levels

i. Interactions of Angular Momenta

While many molecules are closed shell species, with rotational energy levels described in the previous section, most of the species studied in this thesis are radicals. Hence, their rotational energy levels may be complicated by perturbations due to electron spin and orbital, as well as nuclear spin angular momenta. These perturbations can occur through the coupling of the various magnetic moments present within the molecule. For example, the end-over-end rotation of the nuclei can generate a small magnetic moment, $\mu_{\mathrm{Rot}}(\mathrm{R})$. Additionally, the orbiting electron can have an associated a magnetic moment, $\mu_{\mathrm{ORB}}(\mathrm{L})$. Both the electron and nucleus have an intrinsic spin magnetic moment, $\mu_{\text {ESPN }}(\mathrm{S})$ and $\mu_{\text {NUC }}(\mathbb{I})$, respectively. Each of these four magnetic moments may interact and couple to each other (Carrington 1974), as shown in Figure 6, to give eight possible interactions. Because the Bohr (electron) magneton is approximately 1800 times


Figure 6. Magnetic Coupling Interactions of Angular Momenta.
larger than the nuclear magneton (Levine 1991), any coupling involving the electron is expected to be largest. The relative magnitude of the rotational and nuclear spin angular momenta depends on the rotational quantum number as well as the nuclear magnetic moment. Couplings that involve magnetic moments due to the electron are designated as fine structure, while those with the nucleus are referred to as hyperfine. These possible magnetic interactions are summarized in Table 3.

Table 3. Possible Magnetic Angular Momenta Coupling Interactions.

| Coupled Amgular Momenta | Designation |
| :---: | :---: |
| $(\mathbf{R} \cdot \mathbf{S})$ | Spin-Rotation |
| $(\mathbf{L} \cdot \mathbf{S})$ | Spin-Orbit |
| $(\mathbf{I} \cdot \mathbf{S})$ | Fermi Contact and Dipolar Hyperfine |
| $(\mathbf{S} \cdot \mathbf{S})$ | Spin-Spin |
| $(\mathbf{I} \cdot \mathbf{L})$ | Electron Orbital-Nuclear Spin |
| $(\mathbf{R} \cdot \mathbf{L})$ | Lambda Doubling |
| $(\mathbf{I} \cdot \mathbf{R})$ | Nuclear Spin-Rotation |
| $(\mathbf{I} \cdot \mathbf{I})$ | Nuclear Spin-Spin |

Additionally, electric hyperfine effects must be considered. The major interaction of this type arises from nuclear quadrupolar coupling, which is a result of an asymmetric nuclear charge distribution coupling to the external electric potential of the molecule (Townes and Schawlow 1975). In order for a molecule to exhibit quadrupole coupling, it must contain a nucleus with $I>1 / 2$. This interaction is generally largest in the lowest rotational energy levels of a molecule.
ii. Hund's coupling cases

The Hamiltonians required to describe the energy levels of an open shell molecule are much more complicated than Eq. (3.1). In order to evaluate these expressions, a molecular wavefunction must be constructed (Herzberg 1989). This wavefunction can be approximated using a basis set composed of relevant quantum numbers listed in Table 4.

Table 4. Relevant Quantum Numbers in a Diatomic Molecule.

| Quantum Number | Angular Momentum and Relationship |
| :---: | :---: |
| n | Electronic State Label |
| v | Vibrational State |
| R | Rotation |
| L | Electron Orbital |
| S | Electron Spin |
| I | Nuclear Spin |
| $\Sigma$ | Projection of S Onto Internuclear Axis |
| $\mathbf{N}$ | Projection of L onto Internuclear Axis |
| N | Rotation and Electron Orbital: $\mathrm{N}=\mathrm{R}+\mathrm{L}$ |
| J | Total Angular Momentum Excluding Nuclear Spin: $\mathrm{J}=\mathrm{L}+\mathrm{R}+\mathrm{S}$ |
| $\Omega$ | Projection of J onto Internuclear Axis: $\Omega=\Sigma+\Lambda$ |
| F | Total Angular Momentum: $\mathrm{F}=\mathrm{J}+\mathrm{I}$ |

The basis sets can be classified by Hund's coupling schemes (Herzberg 1989). Three of Hund's coupling cases, which depend on the magnitude of the spin-orbit interaction (generally the largest perturbation to the rotational energy levels), will be discussed below.

1. Hund's case(a)

The Hund's case(a) basis set is generally employed to describe molecules with non-zero orbital angular momentum (Herzberg 1989). A schematic of this coupling scheme is shown in Figure 7. As a result of the cylindrical symmetry of a diatomic
molecule, the electron orbital angular momentum is quantized only along the internuclear $(\mathrm{z})$ axis ( $\mathrm{\Lambda}$ ). This results in the strong coupling of the electron spin angular momentum to this axis as well ( $\Sigma$ ). Both the orbital and spin angular momentum can then add as scalars along the axis to form $\Omega$. This interaction is known as spin-orbit coupling.

Additionally, if nuclear spin angular momentum (I) is present, it may couple directly to J vectorally to form $F$. This coupling scheme is known as case ( $a_{\beta}$ ). The possibility exists


Figure 7. Vector Representation of Hund's Coupling Cases ( $a_{\beta}$ ) and $b(\beta \mathrm{~s})$.
that I may be quantized along the internuclear axis and couple to $\Lambda$ and $\Sigma$, however, no example of this case $\left(\mathrm{a}_{\alpha}\right)$ coupling has yet been observed. The basis set for Hund's case $\left(a_{\beta}\right)$ can be expressed in Dirac notation as $|n v \Lambda S \Sigma J \Omega I F\rangle$.

## 2. Hund's case(b)

The Hund's case(b) basis set is generally used to describe molecules in which the orbital angular momentum is essentially zero (Herzberg 1989). A schematic of this coupling scheme is shown in Figure 7. In the absence of orbital angular momentum, the electron spin angular momentum no longer couples to the internuclear axis. The spin angular momentum now couples vectorally, directly to the rotational angular momentum to form J. If nuclear spin is present, it can couple vectorally to J, which is known as case $\left(b_{\beta J}\right)$. Other scenarios for the coupling of I exist; however, these were not encountered in this thesis and will not be discussed. The basis set for Hund's case( $\mathrm{b}_{\beta} \mathrm{J}$ ) can be written as $\mid$ nvNSIIF $\rangle$.
3. Hund's case(c)

A Hund's case(c) coupling scheme is used to describe molecules in which spinorbit coupling is extremely large relative to other angular momenta interactions (Herzberg 1989). In general, it is usually observed in heavy molecules (those containing $3^{\text {rd }}$ row transition metals or lanthanides). In this case $\Lambda$ and $\Sigma$ are no longer good quantum numbers, thus $|n v J \Omega\rangle$ form the appropriate basis set.
iii. Effective Hamiltonians

In order to model the rotational spectrum of an open shell molecule, effective Hamiltonians have been developed (Brown et al. 1978; Brown et al. 1979; Frosch and Foley 1952). For a diatomic molecule this expression can be broken into the following:

$$
\begin{equation*}
\hat{H}_{\mathrm{Bff}}=\hat{H}_{\mathrm{Rot}}+\hat{\mathrm{H}}_{\mathrm{so}}+\hat{\mathrm{H}}_{\mathrm{SR}}+\hat{\mathrm{H}}_{\mathrm{ss}}+\hat{\mathrm{H}}_{\mathrm{LD}}+\hat{\mathrm{H}}_{\mathrm{MHF}}+\hat{H}_{\mathrm{HHF}}+\hat{\mathrm{H}}_{\mathrm{NSR}} \tag{3.5}
\end{equation*}
$$

where

$$
\begin{align*}
& \mathrm{H}_{\mathrm{Rot}}=\mathrm{B} \hat{R}^{2}-\mathrm{DR} \hat{R}^{4}  \tag{3.6}\\
& \mathrm{H}_{\mathrm{SO}}=\mathrm{A} \hat{\mathrm{~L}}_{z} \hat{\mathrm{~S}}_{\mathrm{z}}  \tag{3.7}\\
& \mathrm{H}_{\mathrm{SR}}=\gamma \hat{\mathrm{N}} \cdot \hat{\mathrm{~S}}  \tag{3.8}\\
& \mathrm{H}_{\mathrm{SS}}=2 / 3 \lambda\left(\hat{\mathrm{~S}}_{\mathrm{z}}^{2}-\hat{\mathrm{S}}^{2}\right)  \tag{3.9}\\
& \mathrm{H}_{\mathrm{MHF}}=\mathrm{ai} \hat{\mathrm{I}}_{\mathrm{z}} \hat{\mathrm{~L}}_{\mathrm{z}}+(\mathrm{b}+\mathrm{c}) \hat{\mathrm{I}} \cdot \hat{\mathbf{S}}+\hat{\mathrm{Cl}}_{z} \hat{\mathrm{~S}}_{\mathrm{z}}  \tag{3.10}\\
& \mathrm{H}_{\mathrm{EHF}}=\mathrm{eq}_{0} \mathrm{Q}\left(\hat{\mathrm{I}}_{\mathrm{z}}^{2}-\hat{\mathrm{I}}^{2}\right) / 4 \mathrm{I}(2 \mathrm{I}-1)  \tag{3.11}\\
& \mathrm{H}_{\mathrm{SR}}=\mathrm{C}_{\mathrm{I}} \hat{\mathrm{I}} \cdot \hat{\mathrm{~J}} \tag{3.12}
\end{align*}
$$

and $\mathrm{H}_{\mathrm{LD}}$ describes the lambda-doubling interaction. The constants $A, \gamma, \lambda, a, b, c, e q 0 Q$, and $C_{I}$, are the eigenvalues determined from the effective Hamiltonian. The physical interpretation of each constant as it applies to the types of molecules studied in this thesis are discussed in more detail elsewhere (Brown et al. 1979; Appendices A-K ).

Additionally, each portion of the effective Hamiltonian and the relevant basis sets used to model the rotational data of these molecules will be discussed in more detail in each appendix.

## 3. Fitting Programs

The rotational transition data measured for a particular molecule can be modeled by fitting the data to the appropriate effective Hamiltonian via a list squares fitting program. Matrix elements can be derived from the appropriate molecular Hamiltonian
basis set, allowing for an energy matrix to be calculated for each rotational level. This matrix is then diagonalized and the energy eigenvalues and eigenvectors are determined. The process is iterative and the data is said to be well modeled based on the rms of the fit, in general, when it is less than the experimental accuracy of 100 kHz and based on whether or not the values of the constants are reasonable. In this research, four fitting programs were employed to fit the molecular data. The first, sigalnc, was programmed by A. J. Apponi to fit linear molecules in ${ }^{1} \Sigma$ and ${ }^{2} \Sigma$ states and more importantly to establish harmonic relationships between rotational lines. Hunda and Hundb, written by J. M. Brown and co-workers, were used to fit diatomic molecules in Hund's case (a) and (b) bases. These programs were written in Fortran 90 and were modified several times by the author in order to accommodate additional Hamiltonian terms. Finally, the asymmetric top molecules were fit using Pickett's program, developed by H. M. Pickett and coworkers.

## CHAPTER 4. ALKALI AND ALKALINE-EARTH AMIDES

1. Introduction

Ammonia has played a significant role in the development of rotational spectroscopy (Townes and Schawlow 1975). In particular the hindered motion, inversion, present in the molecule makes it an excellent species to study in the microwave region. It is a natural extension, therefore, to examine ammonia-like compounds, monosubstituted amides $\left(\mathrm{RNH}_{2}\right)$ for example, in order to compare their molecular properties to ammonia. Several such molecules, $\mathrm{NH}_{2} \mathrm{OH}$ (Morino et al. 2000), $\mathrm{NH}_{2} \mathrm{Cl}$ (Cazzoli, Lister, and Favero 1972), $\mathrm{NH}_{2} \mathrm{NC}$ (Schäfer, Winnewisser, and Christiansen 1981), and $\mathrm{NH}_{2} \mathrm{CHO}$ (Costain and Dowling 1960) have been investigated by pure rotational spectroscopy. These species are non-planar and exhibit an inversion spectrum. Their similarity to ammonia is not surprising since the $\mathrm{OH}, \mathrm{Cl}, \mathrm{CN}$, and CHO ligands would be expected to bond covalently to $\mathrm{NH}_{2}$. Metal containing amides, on the other hand, in particular those containing alkali and alkaline-earth metal atoms, may have entirely different molecular properties. For example, an increase in the ionic character of the metal-nitrogen bond might result in a planar structure. Also, the barrier to inversion may increase significantly such that the phenomenon may no longer be observable. Fortunately, millimeter-wave spectroscopy can differentiate between either a pyramidal or planar metal amide as well as detect the presence of inversion.

The alkaline-earth monoamides were first investigated in the gas phase by the Harris group. They successfully recorded the optical spectra of $\mathrm{Ca}, \mathrm{Sr}$, and Ba amides by the reaction of the pure metal vapor with hydrazine (Wormsbecher et al. 1983).

Unfortunately, these spectra were not rotationally resolved and therefore, the authors could only speculate that their geometries were planar. This work was followed by several high-resolution studies of the electronic structure of CaNH , in which the $\widetilde{\mathrm{A}}^{2} \mathrm{~B}_{2}-$ $\widetilde{X}^{2} A_{1}, \widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$, and $\widetilde{\mathbb{C}}^{2} A_{1}-\widetilde{X}^{2} A_{1}$ transitions were recorded (Marr et al. 1995; Morbi et al. 1998; Morbi, Zhao, and Bernath 1997). The rotationally resolved spectra again suggested planarity via the inertial defect. Unfortunately, no isotopomers were studied; therefore the structure could not be determined without assuming an $\mathrm{N}-\mathrm{H}$ bond length. Additionally, high-resolution laser spectroscopic studies of the $\mathrm{SrNH}_{2}$ radical were conducted ( $\widetilde{\mathrm{A}}^{2} \mathrm{~B}_{2}-\widetilde{\mathrm{X}}^{2} \mathrm{~A}_{1}, \widetilde{\mathrm{~B}}^{2} \mathrm{~B}_{1}-\widetilde{\mathrm{X}}^{2} \mathrm{~A}_{1}$ ) (Brazier and Bernath 2000). Again, the data suggested a planar structure. No pure-rotational spectra had been recorded for any of these species.

The first metal amide to be studied by millimeter-wave spectroscopy was $\mathrm{NaNH}_{2}$ (Xin, Brewster, and Ziurys 2000). This species was of particular interest from an astrochemical standpoint, as metal amides were postulated to form in the circumstellar envelopes of late-type stars (Petrie 1996). The presence of $\mathrm{NH}_{3}$ (Truong-Bach, Nguyen-Q-Rieu, and Graham 1988), as well as the sodium bearing species NaCN and NaCl (Highberger et al. 2003), made sodium amide an excellent candidate for interstellar detection. Structurally this species was found to be planar, with no evidence for inversion. This work was followed by the observation of the millimeter-wave spectrum of $\mathrm{CaNH}_{2}$ and its deuterium isotopomer $\mathrm{CaND}_{2}$ (Brewster and Ziurys 2000). Both of these species were determined to be planar, and the first $r_{0}$ structure of a metal amide was determined. Subsequently, pure rotational transitions of $\mathrm{MgNH}_{2}, \mathrm{MgND}_{2}, \mathrm{LiNH}_{2}$,
$\mathrm{LiND}_{2}, \mathrm{NaND}_{2}, \mathrm{SrNH}_{2}$, and $\mathrm{SrND}_{2}$ were recorded and analyzed in this thesis. The results of these investigations will be summarized in the remaining portion of this chapter.
2. Theory of Asymmetric Tops

The rotational energy levels of a molecule depend on the geometric and electronic structure of the molecule (Townes and Schawlow 1975; Bernath 1995). If the metal amides are planar, then they belong to the $\mathrm{C}_{2 \mathrm{v}}$ point group, while if they are pyramidal, they have $\mathrm{C}_{\mathrm{s}}$ symmetry. Both the planar and pyramidal $\mathrm{MNH}_{2}$ species are classified as asymmetric top molecules, since for each no two principal moments of inertia are equal


Figure 8. Molecular Axis Labeling in $\mathrm{MNH}_{2}$.
( $I_{A}<I_{B}<I_{C}$ ). The classification of asymmetric rotors is based on their similarity to the symmetric top species: prolate $\left(I_{A}<I_{B}=I_{C}\right)$ or oblate $\left(I_{A}=I_{B}<I_{C}\right)$. Using the molecular axis labeling in Figure 8 (Appendix C), the metal amides would be considered nearprolate asymmetric tops. In a symmetric top species, the projection of the rotational angular momentum, $\mathbb{K}$, onto the molecular symmetry axis must be considered. In an asymmetric top the $\mathbb{K}$ energy levels are no longer degenerate; their splitting is determined
by the degree of asymmetry of the molecule. An energy level correlation diagram illustrating the prolate and oblate symmetric top species as limiting cases of the asymmetric rotor is shown in Figure 9. In an asymmetric top the non-degenerate $K$ components are labeled as $\mathrm{K}_{\mathrm{a}}$ and $\mathrm{K}_{\mathrm{c}}$. Unfortunately, these quantum labels do not correspond to a particular projection axis and are only good in the oblate and prolate limiting cases. As one moves towards the center of this diagram (most asymmetric) the splitting of the $K$ levels increases. Selection rules for transitions between the rotational


Figure 9. Correlation Energy Diagram for an Asymmetric Top.
energy levels of an asymmetric top molecule are given by the electric dipole moment operator. For an asymmetric top, the electric dipole moment can be divided into non-zero components along the principle axes, and this must be taken into consideration in deriving selection rules. For the most intense rotational transitions, the selection rule is $\Delta J=+1$ (in absorption), while those for $K_{\mathrm{a}}$ and $\mathrm{K}_{\mathrm{c}}$ levels are summarized in Table 5

Table 5. Asymmetric Top Selection Rules.

|  | $\hat{a}$ - dipole | $\hat{b}$-dipole | $\hat{c}$ - dipole |
| :--- | :---: | :---: | :---: |
| $\Delta \mathbf{K}_{\mathrm{a}}$ | 0 | $\pm 1$ | $\pm 1$ |
| $\Delta \mathrm{~K}_{\mathrm{c}}$ | $\pm 1$ | $\pm 1$ | 0 |

(Bernath 1995). In the case of either the planar or pyramidal amides, â-dipole transitions would be expected to be most intense as this would be the largest non-zero component of the dipole moment (see Figure 8). For the pyramidal amide, however, a small $\hat{c}$-dipole moment also arises resulting in weak c-type transitions.

One major difference between the pyramidal and planar metal amides is the $\mathrm{C}_{2}$ rotation axis. The planar molecule, unlike the pyramidal contains this symmetry element. A rotation of the planar species about the $\mathrm{C}_{2}$ axis results in an exchange of the two protons. Since the two protons are both fermions, this exchange must be antisymmetric with respect to the total molecular wavefunction,

$$
\begin{equation*}
\Psi_{\text {Tot }}=\Psi_{\text {Electronic }} \Psi_{\text {Vibrational }} \Psi_{\text {Rotational }} \Psi_{\text {NuclearSpin }} \tag{4.1}
\end{equation*}
$$

The electronic and vibrational wavefunctions of the molecule are symmetric since the molecule has $\mathrm{A}_{1}$ symmetry in its ground state. The symmetry of the rotational wavefunction is given by $e^{-i K_{a} \phi}$; therefore, for even $K_{a}$ values $\Psi_{\text {Rot }}$ is symmetric(sym) and for odd $\mathrm{K}_{\mathrm{a}}$ values $\Psi_{\text {Rot }}$ is antisymmetric(asym). Thus, in order for $\Psi_{\text {Tot }}$ to be antisymmetric, $\Psi_{\text {Rot }}$ (asym) must be accompanied by $\Psi_{\text {Nuc }}$ (sym:ortho) and $\Psi_{\text {Rot }}$ (sym) with $\Psi_{\text {Nuc }}$ (asym:para). Four nuclear spin wavefunctions can be constructed for the two fermions; three are symmetric while one is antisymmetric (ortho:(I+1)(2I+1); para: $1(2 I+1)$ )(Townes and Schawlow 1975). As a result, a nuclear spin-weighting factor
must be considered in the intensities of the $\mathrm{K}_{\mathrm{a}}$ components in the rotational spectrum of the planar amide. This results in the odd $\mathrm{K}_{\mathrm{a}}$ components having an intensity ratio of 3:1 relative to the even $\mathrm{K}_{a}$ components (excluding Boltzmann distribution factors). In the deuterium species, $\mathrm{MND}_{2}$, the exchange of the deuterons results in a $2: 1$ intensity enhancement of $\mathrm{K}_{\mathrm{a}}$ (even) to $\mathrm{K}_{\mathrm{a}}$ (odd). Since the pyramidal species does not have a $\mathrm{C}_{2}$ axis, nuclear spin statistics will not be present (unless it is inverting then each of the two inversion states will exhibit opposite spin statistics). The intensity enhancement of the $\mathrm{K}_{\mathrm{a}}$ components by nuclear spin statistics presents an excellent method for distinguishing between the planar and pyramidal species via rotational spectroscopy.

The symmetry of the ground electronic state of a molecule is determined by the electronic wavefunction. For alkali and alkaline-earth containing molecules, this can be determined by considering the ligand as a point charge perturbation on the metal ion (Rittner 1951). In this case, the symmetry of the electronic wavefunction can be determined by the ground state term of the ion. For the alkali metals, this term is ${ }^{1} \mathrm{~S}$ and for the alkaline-earth metals it is ${ }^{2} \mathrm{~S}$. Taking into account the overall geometry of the molecule, the correlation tables between point groups can be used to determine the molecular symmetry. In the $\mathrm{C}_{2 \mathrm{v}}$ point group, the alkali amides have ${ }^{1} \mathrm{~A}_{1}$ and the alkalineearth amides have ${ }^{2} \mathrm{~A}_{1}$ ground states. For the pyramidal species $\left(\mathrm{C}_{5}\right)$, the alkali-amides have ${ }^{1} \mathrm{~A}$ ' and the alkaline-earth amides have ${ }^{2} \mathrm{~A}^{\prime}$ ground state terms.

Finally, the presence of inversion must be considered. This phenomenon will manifest itself by splitting the rotational spectrum into two inversion components separated by a small amount in frequency space as in $\mathrm{NH}_{2} \mathrm{NC}$ (Schäfer, Winnewiser, and

Christiansen 1981). In one inversion component the nuclear spin statistics will appear reversed, thus the intensity ratio will be $3: 1 \mathrm{~K}_{\mathrm{a}}$ (even): $\mathrm{K}_{\mathrm{a}}$ (odd). Unfortunately, the rotational spectrum of the $\mathrm{v}_{4}$ symmetric stretch will appear similar to the inversion spectrum. Care must be taken not to confuse the two phenomena (the rotational spectrum of the $\mathrm{v}_{4}$ mode should generally be less intense than that of an inversion component).

## 3. Results

The spectroscopic results for each of the amides studied in this thesis can be found in more detail in Appendices A-D. Here they will be summarized briefly. The measurement of the pure rotational spectra of $\mathrm{MgNH}_{2}, \mathrm{MgND}_{2}, \mathrm{LiNH}_{2}, \mathrm{LiND}_{2}, \mathrm{NaND}_{2}$, and $\mathrm{SrND}_{2}$ represent the first detection of these species in the gas phase by any spectroscopic method. Therefore, large frequency ranges ( $\sim 50-150 \mathrm{GHz}$ ) were scanned in order to assign spectral features due to each amide (assignment details can be found in Appendices A-D; Brewster and Ziurys 2000). Only a-type transitions were detected for each amide. In addition nuclear spin statistics were observed in each rotational spectra. Representative laboratory and stick spectra for each amide can be found in Appendices A-D. For each molecule, there was no evidence for an inversion spectrum. Therefore, each species was determined to be planar and non-inverting with $\mathrm{C}_{2 v}$ symmetry. Measured rotational transitions for each amide can also be found in Appendices A-D.
4. Analysis

The pure rotational transition data of the metal amides were fit using Watson's Sreduced Hamiltonian for asymmetric tops (Watson 1977). The form of this Hamiltonian, with higher order notation is:

$$
\begin{align*}
& \mathrm{H}_{\mathrm{Rot}}^{(\mathrm{s})}=\mathrm{AN}_{\mathrm{x}}^{2}+\mathrm{BN}_{\mathrm{y}}^{2}+\mathrm{CN}_{\mathrm{z}}^{2}-\mathrm{D}_{\mathrm{N}} \mathrm{~N}^{4}-\mathrm{D}_{\mathrm{NK}} \mathrm{~N}^{2} \mathrm{~N}_{\mathrm{z}}^{2}-\mathrm{D}_{\mathrm{K}} \mathrm{~N}_{\mathrm{z}}^{4}+\mathrm{d}_{1} \mathrm{~N}^{2}\left(\mathrm{~N}_{+}^{2}+\mathrm{N}_{-}^{2}\right) \\
& +\mathrm{d}_{2}\left(\mathrm{~N}_{+}^{4}+\mathrm{N}_{-}^{4}\right)+\mathrm{H}_{\mathrm{N}} \mathrm{~N}^{6}+\mathrm{H}_{\mathrm{NK}} \mathrm{~N}^{4} \mathrm{~N}_{\mathrm{z}}^{2}+\mathrm{H}_{\mathrm{KN}} \mathrm{~N}^{2} \mathrm{~N}_{\mathrm{z}}^{4}+\mathrm{H}_{\mathrm{K}} \mathrm{~N}_{\mathrm{z}}^{6}+h_{1} \mathrm{~N}^{4}\left(\mathrm{~N}_{+}^{2}+\mathrm{N}_{-}^{2}\right) \\
& +\mathrm{h}_{2} \mathrm{~N}^{2}\left(\mathrm{~N}_{+}^{4}+\mathrm{N}_{-}^{4}\right)+\mathrm{h}_{3}\left(\mathrm{~N}_{+}^{6}+\mathrm{N}_{-}^{6}\right)+\mathrm{L}_{\mathrm{N}} \mathrm{~N}^{8}+\mathrm{L}_{\mathrm{NNK}} \mathrm{~N}^{6} \mathrm{~N}_{\mathrm{z}}^{2}+\mathrm{L}_{\mathrm{NK}} \mathrm{~N}^{4} \mathrm{~N}_{\mathrm{z}}^{4}  \tag{4.2}\\
& +\mathrm{L}_{\mathrm{KKN}} \mathrm{~N}^{2} \mathrm{~N}_{z}^{6}+\mathrm{L}_{\mathrm{K}} \mathrm{~N}_{\mathrm{z}}^{8}+\mathrm{P}_{\mathrm{N}} \mathrm{~N}^{10}+\mathrm{P}_{\mathrm{NK}} \mathrm{~N}^{8} \mathrm{~N}_{\mathrm{z}}^{2}+\mathrm{P}_{\mathrm{NNK}} \mathrm{~N}^{6} \mathrm{~N}_{\mathrm{z}}^{4}+\mathrm{P}_{\mathrm{NKK}} \mathrm{~N}^{4} \mathrm{~N}_{\mathrm{z}}^{6} \\
& +\mathrm{P}_{\mathrm{KN}} \mathrm{~N}^{2} \mathrm{~N}_{\mathrm{z}}^{8}+\mathrm{P}_{\mathrm{K}} \mathrm{~N}_{\mathrm{z}}^{10}
\end{align*}
$$

where $A, B$, and $C$ are the rotational constants corresponding to each principle molecular axis and the remaining terms describe centrifugal distortion corrections. In Eq. (4.2), the operators are given in terms of $\mathbf{N}$ where $\mathbb{J}=\mathbf{N}+\mathbf{S}$. For the alkali metal amides $\mathbf{S}=0$ and $N$ is replaced with $\mathbb{J}$. For the alkaline-earth amides $S=1 / 2$ due to the single unpaired electron present. This results in a fine structure interaction, spin-rotation coupling, which can be modeled by inclusion of the following term (Brown and Sears 1979)

$$
\begin{equation*}
H_{s T}=\sum_{\alpha} \varepsilon_{\alpha \alpha} N_{\alpha} \cdot S_{\alpha}+\Delta_{\mathrm{NK}}^{\mathrm{S}}(N \cdot S) N^{2} N_{z}^{2} \tag{4.3}
\end{equation*}
$$

where $\alpha$ sums over the three molecular axes, $\varepsilon_{\alpha \alpha}$ is the spin-rotation constant, and $\Delta_{\mathrm{NK}}^{\mathrm{s}}$ is a centrifugal distortion correction. Since the metal amides have orthorhomic symmetry $\left(\mathrm{C}_{2 \mathrm{v}}\right)$ only diagonal components of the spin-rotation tensor are non-zero. The spectroscopic parameters determined for each species can be found in Appendices A-D.
5. Discussion
i. Case for Planarity

The presence of nuclear spin statistics in the pure rotational spectra of the metal amides indicates these species are planar. Additional evidence for planarity arises from the inertial defect of the molecule, $\Delta_{0}=I_{C}-I_{B}-I_{A}$. A molecule has a non-zero inertial defect due to vibrational, electronic, and centrifugal distortion effects (Oka and Morino
1961). In general a small positive value of $\Delta_{0}$ indicates planarity as for formaldehyde, which has an inertial defect of 0.05767 amu $\AA^{2}$ (Clouthier and Ramsey 1983). Negative or large values are interpreted as signs of nonplanar or fluxional behavior. The inertial defects of the metal amides are presented in Table 6. These values are all small and

Table 6. Inertial Defects for Selected Amides.

| Molecule | $\Delta_{0}\left(a m u \AA^{2}\right)$ |
| :---: | :---: |
| $\mathrm{LiNH}_{2}$ | 0.115 |
| $\mathrm{LiND}_{2}$ | 0.150 |
| $\mathrm{NaNH}_{2}$ | 0.079 |
| $\mathrm{NaND}_{2}$ | 0.110 |
| $\mathrm{MgNH}_{2}$ | 0.078 |
| $\mathrm{MgND}_{2}$ | 0.096 |
| $\mathrm{CaNH}_{2}$ | 0.157 |
| $\mathrm{CaND}_{2}$ | 0.210 |
| $\mathrm{SrNH}_{2}$ | 0.177 |
| $\mathrm{SrND}_{2}$ | 0.242 |
| $\mathrm{NH}_{2} \mathrm{OH}$ | -2.600 |
| $\mathrm{NH}_{2} \mathrm{Cl}$ | -1.032 |
| $\mathrm{NH}_{2} \mathrm{CHO}$ | 0.008 |
| $\mathrm{ND}_{2} \mathrm{CHO}$ | -0.015 |

positive, very similar to that of formaldehyde. For comparison, the inertial defects of additional amides are shown in Table 6. The inertial defects of $\mathrm{NH}_{2} \mathrm{OH}$ and $\mathrm{NH}_{2} \mathrm{Cl}$ are both negative as both molecules are pyramidal. For formamide $\Delta_{0}$ is small and positive, which would indicate a planar geometry. However, on deuterium substitution, the inertial defect becomes negative indicating a non-planar structure. For the deuterium substituted amides all of the inertial defects are small and positive.

## ii. Structure

The pure rotational spectra of the deuterium isotopomers of each metal amide were measured in order to determine $r_{0}$ structures. From the rotational constants of each molecule, the principle moments of inertia were calculated and the structural parameters determined by (Gordy and Cook 1984):

$$
\begin{gather*}
I_{A}=2 m_{H} r_{N H}^{2} \sin (\theta / 2)^{2} \\
\left.I_{B}=1 / M \mid m_{H}\left(2 m_{H}+m_{N}\right) r_{M N}^{2}+2 m_{H}\left(m_{N}+m_{M}\right) r_{N H}^{2} \cos (\theta / 2)^{2}+4 m_{H} m_{M} \mathrm{r}_{\mathrm{MN}} r_{N H} \cos (\theta / 2)\right] \\
I_{C}=I_{A}+I_{B} \tag{4.4}
\end{gather*}
$$

A least squares fitting routine was employed in order to determine the bond lengths and bond angle for each molecule are listed in Table 7.

Table 7. Structural Parameters of the Metal Amides.

|  | $\mathrm{r}_{0 \mathrm{M}-\mathrm{N}}(\AA)$ | $\mathrm{r}_{0 \mathrm{~N}-\mathrm{H}}(\AA)$ | $\theta_{\mathrm{H}-\mathrm{N}-\mathrm{H}}{ }^{\circ}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{LiNH}_{2}$ | $1.736(1)$ | $1.022(1)$ | $106.9(1)$ |
| $\mathrm{NaNH}_{2}$ | $2.091(1)$ | $1.008(1)$ | $106.6(1)$ |
| $\mathrm{MgNH}_{2}$ | $1.899(1)$ | $1.007(1)$ | $108.7(1)$ |
| $\mathrm{CaNH}_{2}$ | $2.126(1)$ | $1.018(1)$ | $105.8(1)$ |
| $\mathrm{SNNH}_{2}$ | $2.256(1)$ | $1.021(1)$ | $105.5(1)$ |
| $\mathrm{NH}_{3}$ |  |  | $120^{\text {a) }}$ |

a) Angle projected onto plane defined by H atoms.

The M-N bond length decreases from Sr to Ca to Mg and from Na to Li , consistent with decreasing atomic radius as one moves up the periodic table. The N-H bond length remains fairly constant at $1.01-1.02 \AA$ for each molecule. However, the H-N-H bond angle for $\mathrm{MgNH}_{2}$, is approximately two to three degrees larger than the other metal amides. The increase in $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle may indicate that $\mathrm{MgNH}_{2}$ is tending towards a pyramidal structure, with $\mathrm{BeNH}_{2}$ possibly having a non-planar geometry. A more
detailed discussion of this structural change as well as ionic and covalent character in the metal-nitrogen bond can be found in Appendix B. It should be noted that attempts at measuring the pure rotational spectra of $\mathrm{BaNH}_{2}$ and $\mathrm{ANH}_{2}$ were not met with success.

## CHAPTER 5. DIATOMICS IN HIGH ANGULAR MOMENTUM STATES

1. Introduction

The spectra of diatomic molecules containing transition metals can be quite complicated. These complications arise from the large number of unpaired delectrons that may be present on the metal atom. The result is often many low-lying electronic states with high values of electron spin and orbital angular momenta that can perturb the ground state. Additionally, several of the first row transition metals contain large values of nuclear spin angular momentum, I, and large nuclear magnetic moments, further convoluting the molecular spectra. Thus, the study of transition metal diatomics can be quite arduous.

Despite the difficulties in analyzing the spectra of diatomic molecules in high angular momenta states, many have been studied in detail. Table 8 shows the ground states of the species formed between the 3 d transition metals and some common one atom ligands.

Table 8. Ground States of Diatomic 3d Transition Metal Molecules.

|  | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| H | 18 | $\omega_{r}$ | ${ }^{5} \Delta_{r}$ | ${ }^{6}{ }^{5}$ | \% | ${ }^{4}$ | ¢ | ${ }^{2}{ }^{\text {, }}$ | ${ }^{1} \Sigma^{+}$ | ${ }^{2} \Sigma^{4}$ |
| F | ${ }^{1} \Sigma^{+}$ | ${ }^{\text {¢ }}$ | $\Delta_{\text {r }}$ | ${ }^{6}{ }^{5}+$ | 5 | ${ }^{6} \Delta_{i}$ | $\varphi_{1}$ | ${ }^{2}{ }^{1}{ }_{1}$ | ${ }^{1} \Sigma^{+}$ | ${ }^{2} \Sigma^{+}$ |
| Cl | ${ }^{1} \Sigma^{+}$ | 6 | ${ }^{\text {A }}$ | ${ }^{6} \Sigma^{+}$ | 287 | ${ }^{6} \Delta_{i}$ | \% ${ }^{6}$ | ${ }^{2}{ }_{14}$ | ${ }^{1} \Sigma^{+}$ | ${ }^{2} \Sigma^{+}$ |
| 0 | ${ }^{2}$ | ${ }^{3} \Delta_{r}$ | ${ }^{4} \Sigma^{*}$ | $\Pi$ | ${ }^{6} \Sigma^{+}$ | ${ }^{5}{ }^{4}$ | ${ }^{4} \Delta_{i}$ | ${ }^{3} \Sigma$ | ${ }^{2}{ }^{1}$ | ${ }^{1} \Sigma^{+}$ |
| S | ${ }^{24}$ | ${ }^{\text {\% }}$ | 2 | ${ }^{5} \Pi_{\text {r }}$ | ${ }^{6} \Sigma^{+}$ | ${ }^{5} \Delta_{i}$ | ${ }^{4} \Delta_{i}$ | ${ }^{3} \Sigma^{-}$ | $\left.{ }^{2}\right]_{i}$ | ${ }^{1} \Sigma^{+}$ |
| N | $\underline{1}$ | ${ }^{2} \Sigma^{+}$ | ${ }^{3} \Delta_{r}$ | 15 | -- | P | ${ }^{1} \Sigma^{+}$ | ${ }^{4} \Sigma^{-}$ | ${ }^{3} \Sigma$ | ${ }^{4} \Sigma^{5}$ |
| C | ${ }^{2} \Pi$ | ${ }^{3} \Sigma^{+}$ | ${ }^{2} \Delta_{T}$ | ${ }^{3} \Sigma^{-}$ | - | , | ${ }^{2} \Sigma^{4}$ | ${ }^{1} \Sigma^{+}$ | -- | ${ }^{3} \Sigma$ |

24: Gas Phase Detection by Optical Spectroscopy
${ }^{1} \Sigma^{+}$: Theoretical Studies or Assumed Ground State
${ }^{1} \Sigma^{+}$: Microwave Spectrum Recorded
IE: Microwave Spectrum Recorded in this Dissertation

Immediately it can be observed from this table that greater than one-third of these molecules have not yet been observed by any experimental method, thus their ground states have not yet been conclusively assigned. Also, only one-third have been observed at high resolution by microwave spectroscopy. Many of the ground states of the molecules in Table 8 have high electron orbital and spin angular momentum. Several states with $\Delta$ and $\Phi$ terms as well as those with quartet and higher spin multiplicities have been seldom observed. Therefore, measurement of the pure rotational spectra of molecules in these states serves to test the Hamiltonians developed for them including any higher order parameters. From Table 8 it can be seen that the 3 d transition metal oxides have been studied in the greatest detail (Merer 1989). From these investigations structural and bonding trends have been established for these species. However, for other ligands, a similar thoroughness does not exist. Additional high-resolution spectroscopic investigations are necessary in order to establish the same trends. Thus, not only are these metal containing molecules of interest because of their high-spin ground states, but also in obtaining chemical trends for a particular metal-ligand species. Finally, sufficient interstellar abundances of the transition metals suggest that several of these molecules may be present in the interstellar medium (Anders and Grevesse 1989).
2. Theory
i. Molecular Orbital Approach

The general theory for diatomic molecules has been presented in Chapter 3; therefore a molecular orbital approach to interpreting the properties of these molecules will be discussed. It must be noted that only the electronic states of a molecule are
solutions to the Schroedinger equation, while the molecular orbitals serve only as an interpretation of this solution (Merer 1989). The energy ordering of these orbitals can be estimated from the energies of the atomic orbitals of the individual atoms. However, because of the electrons, this ordering and especially their electron filling is difficult to predict. High level calculations, which explicitly take into account electron correlation effects, coulomb splittings, and configuration interaction are required to accurately determine their electronic and geometric structure. Unfortunately these calculations are time consuming and not yet available for every molecule.

In the absence of $a b$ initio calculations, molecular orbital diagrams can be approximated in order to interpret the bonding and structural properties of a molecule. For example, from the spectroscopic data of the 3 d transition metal oxides the qualitative molecular orbital diagrams shown in Figure 10 have been constructed (Merer 1989). In fact they provide a general model for the other 3d transition metal diatomics, if the energies of the ligand orbitals are adjusted accordingly (those of the metal hydrides will be much different and they will not be discussed here). In Figure 10, the $8 \sigma$ and $3 \pi$ orbitals are bonding orbitals, the $9 \sigma$ and $1 \delta$ are non-bonding metal centered orbitals, and the $4 \pi$ and $10 \sigma$ orbitals are predominately anti-bonding and metal centered in character. The energies of the molecular orbitals can be seen to shift as one moves to the right of the 3 d row. This shift is the result of the energy of the metal orbitals dropping relative to the ligand orbitals, and the 3 d metal orbital energy dropping relative to the 4 s orbital. The filling scheme of the electrons is for the $8 \sigma$ and $3 \pi$ orbitals become occupied, followed by additions to the $9 \sigma, 18,4 \pi$, and $10 \sigma$ orbitals in a non-Aufbau manner. This results in


Ti


0


Cl
0

Figure 10. Qualitative Molecular Orbital Diagrams for Transition Metal Oxides.
a maximum spin multiplicity occurring for manganese and chromium containing molecules, which is not unexpected as Mn and Cr atoms have ${ }^{7} \mathrm{~S}$ and ${ }^{6} \mathrm{~S}$ ground states terms. In Figure 10, the molecular orbitals are shown close in energy. The difficulty in predicting or calculating the energies of these orbitals is the primary reason for the ambiguity associated with determining the electronic term of the ground state (as well as those of the excited state manifold) of the molecule. For this reason, experimental methods must be used to ultimately determine the electronic state terms. Unfortunately, even experiments can be misleading. Incorrect assignments can result due to the complex spectra, perturbations between electronic states, and the type of experiment preformed. For example, the ground state of TiF was first assigned as ${ }^{4} \Sigma$, then ${ }^{2} \Delta$, and finally confirmed as ${ }^{4} \Phi$, over a period of 30 years (Appendix I). Millimeter-wave spectroscopy is particularly useful in confirming the ground state of a molecule as rotational transitions are recorded in the ground electronic state in these experiments. However, even this technique is not without drawbacks as the large spin-orbit coupling associated with many transition metal diatomics can result in dubious assignments.

## ii. Higher Order Terms

High angular momenta ground states may require additional terms in perturbation theory to accurately describe their spectra at high resolution. The advent of high resolution lasers and millimeter-wave spectroscopic techniques has lead to the need to model experimental data using these terms. Budo and Kovacs (1948) showed that the spin-rotation and spin-spin interactions could be obtained solely from a perturbation expansion of the spin-orbit Hamiltonian. Hougen (1962) applied their method to a more general treatment of the energy levels of molecules in ${ }^{4} \Sigma$ states. He presented for the first time a $3^{\text {rd }}$ order spin-orbit correction term to the spin-rotation interaction and suggested that a similar treatment for molecules in higher spin states would result in additional higher order terms. He generalized that for states of even spin multiplicity that ( $\mathrm{S}-1 / 2$ ) parameters for the spin-spin interaction $(\lambda)$ and $(\mathrm{S}+1 / 2)$ parameters for the spin-rotation interaction $(\gamma)$ would be necessary. For states of odd multiplicity he postulated that S parameters analogous to $\lambda$ and $\gamma$ would be necessary.

The first of the higher order parameters to appear in its current form was the third order correction to the spin-rotation interaction, $\gamma_{s}$. The authors stated that the parameter would only be necessary in cases of high resolution or where nearby electronic states interact strongly via spin orbit coupling (Brown and Milton 1976). It has the case (b) form:

$$
\begin{equation*}
\mathrm{H}_{\mathrm{sr}}^{3}=(10 / \sqrt{6}) \gamma_{\mathrm{s}} \mathbf{T}^{3}\left(\mathbf{L}^{2}, \mathbf{N}\right) \mathbf{T}^{3}(\mathbf{S}, \mathbf{S}, \mathbf{S}) \tag{5.1}
\end{equation*}
$$

Additionally these authors developed the fourth order spin-orbit correction, $\theta$, which is a higher order spin-spin interaction term. The form of this term is given as:

$$
\begin{equation*}
H_{s s}^{(4)}=\frac{\theta}{12}\left[35 S_{z}^{4}-30 S^{2} S_{z}^{2}+25 S_{z}^{2}-6 S^{2}+3 S^{4}\right] \tag{5.2}
\end{equation*}
$$

The $\gamma_{s}$ term can only be used for states of quartet or higher multiplicity, while $\theta$ is limited to states of quintet or higher multiplicity. Additional terms for higher order spin-orbit correction have not yet been developed due to the lack of their necessity in modeling systematic errors in fitting data. The higher order parameter, $\eta$, was developed to fill such a need in the fitting of spectral data for $\mathrm{O}_{2}{ }^{+}$(Brown et al. 1981). This term

$$
\begin{equation*}
H_{\mathrm{so}}^{(3)}=\eta \mathrm{L}_{\mathrm{z}} \mathrm{~S}_{\mathrm{z}}\left(\mathrm{~S}_{\mathrm{z}}^{2}-\frac{3 \mathrm{~S}^{2}-1}{5}\right) \tag{5.3}
\end{equation*}
$$

accounts for the coupling of the spin-orbit and spin-spin interactions via third order perturbation theory. In general, while these terms have been developed and tested to some degree by optical spectroscopy, higher resolution microwave spectroscopic measurements of molecules in high spin states have been limited. Several of the diatomic molecules studied in this thesis have been used to test the necessity of these higher order parameters.

## 3. Results of High Spin Molecules

Several molecules in high spin ground states have been investigated in this thesis. The results of these studies will be summarized in this section by ground state. Details can be found in Appendices $\mathrm{E}, \mathrm{F}, \mathrm{H}, \mathrm{I}$, and J.
i. $\mathrm{NaC}\left(\mathrm{X}^{4} \Sigma\right)$ and $\mathrm{CrN}\left(\mathrm{X}^{4} \Sigma\right)$

Only three molecules with ${ }^{4} \Sigma$ ground states have been studied by millimeter wave spectroscopy to date, KC (Xin and Ziurys, 1999), NaC , and $\mathrm{CrN} . \mathrm{NaC}$ is the only nontransition metal diatomic studied in this thesis since few alkali and alkaline-earth containing molecules tend to exhibit high spin ground states. The pure rotational transitions of each of these molecules provide an excellent example of how varied the rotational spectra of the same ground state can appear. Figure 11, shows a representative rotational spectrum of each of these species in the $460-485 \mathrm{GHz}$ region. In the top panel the four fine structure components of the $\mathrm{N}=27 \rightarrow 28$ rotational transition of KC are shown, clearly resolved and almost equally spaced. In the middle panel, the $\mathrm{N}=17 \rightarrow 18$ rotational transition of NaC is shown. Here only three features are present, however, the middle one appears to be more intense. For NaC the middle two fine structure components are not resolved. Finally, in the bottom panel the four spin components of the $\mathrm{N}=13 \leftarrow 12$ of CrN are shown. While each is well-resolved, they are not split evenly in frequency space (note the 1.4 GHz frequency gap in the spectrum). The differences in each of the three spectra arise from the magnitude of the spin-spin and spin-rotation interactions. Table 9 lists the spectroscopic parameters determined for these three species. For all three molecules the value of $\lambda$ is greater than $\gamma$, however for KC and NaC the value of $\lambda$ is only 35 and 23 times larger than $\gamma$, while for CrN it is 375 times greater. The small magnitude of both fine structure constants in NaC leads to the unresolved nature of the middle spin components. Appendix E contains simplified energy level expressions for the spin-components of a ${ }^{4} \Sigma$ molecule. From these equations

Table 9. Spectroscopic Parameters for $\mathrm{NaC}, \mathrm{KC}$, and CrN .

| Parameter | $\mathrm{NaC}\left(\mathrm{X}^{4} \Sigma^{-}\right)$ | $\mathrm{KC}\left(\mathrm{X}^{4} \Sigma^{-}\right)$ | $\mathrm{CrN}\left(\mathrm{X}^{4} \Sigma^{-}\right)$ |
| :---: | :---: | :---: | :---: |
| B | $12863.1243(26)$ | $8619.8946(77)$ | $18702.9105(12)$ |
| D | $0.048564(41)$ | $0.021779(12)$ | $0.0318625(27)$ |
| $\gamma$ | $3.23(38)$ | $5.34(10)$ | $208.897(36)$ |
| $\gamma_{\mathrm{D}}$ | - | $-0.000141(42)$ | $0.00067(50)$ |
| $\lambda$ | $135(45)$ | $248(17)$ | $78287.04(41)$ |
| $\lambda_{\mathrm{D}}$ | $0.0040(87)$ | $0.00141(40)$ | $-0.22088(44)$ |
| rms | 0.646 | 0.044 | 0.197 |
|  |  |  |  |
| B | $12863.1344(54)$ | $8619.8965(64)$ | $18702.9055(14)$ |
| D | $0.0485764(85)$ | $0.0217807(99)$ | $0.0318543(32)$ |
| $\gamma$ | $2.710(91)$ | $5.04(21)$ | $209.261(47)$ |
| $\gamma_{\mathrm{D}}$ | -- | $-0.000063(62)$ | $0.000291(64)$ |
| $\gamma_{\mathrm{S}}$ | $-0.455(42)$ | $-0.0521(35)$ | $0.1328(85)$ |
| $\lambda$ | $57.5(11.5)$ | $175(51)$ | $78281.97(58)$ |
| $\lambda_{\mathrm{D}}$ | $0.0043(18)$ | $0.001444(32)$ | $-0.21744(56)$ |
| rms | 0.132 | 0.036 | 0.023 |

it can be seen that the effect of spin-spin coupling diminishes in importance at higher N while the spin-rotation interaction increases. The large uneven separation of the fine structure components in CrN is a result of the large value of $\lambda$. At higher N , these spin components will have a more even splitting as $\gamma$ again dominates (see Appendix F).

One other interesting anomaly discovered in the fitting of quartet sigma molecules concerns an ambiguity in the determination of the value of $\lambda$. In the original fit of the rotational transition data of KC , the value of the spin-spin interaction was found to be large ( 17.0 GHz ). However, in the fitting of the NaC data it was found that two values of $\lambda$ could be obtained with near identical values of the rms of the fit ( 64.4 MHz and 25.7

GHz ). This fitting ambiguity and the reasons for choosing the smaller value of $\lambda$ in KC and NaC is discussed in detail in Appendix E.


Figure 11. Laboratory Spectra of $\mathrm{KC}, \mathrm{NaC}$, and $\mathrm{CrN}(460-485 \mathrm{GHz})$.

In Table 9, fits of the rotational transition data of $\mathrm{NaC}, \mathrm{KC}$, and CrN to a ${ }^{4} \Sigma$ Hamiltonian with and without the $\gamma_{s}$ term are shown. For each molecule, the rms value of the fit decreased with the inclusion of $\gamma_{s}$. Therefore, in the case of the high resolution
millimeter wave data of $\mathrm{NaC}, \mathrm{KC}$, and CrN , the third order spin-rotation term postulated by Hougen over 40 years was found to be necessary to correctly model the data.

Measured rotational transition frequencies of NaC and CrN can be found in Appendices E and F .
ii. $\mathrm{CrO}\left(\mathrm{X}^{5} \Pi_{r}\right)$

The observation of the CrO radical by millimeter wave spectroscopy represents the first measurement of the rotational spectrum of a molecule in a ${ }^{5} \Pi$ state. The radical was subject to several previous spectroscopic investigations, including the measurement


Figure 12. Qualitative Energy Level Diagram for a ${ }^{5} \Pi$ State.
of the ${ }^{5} \Sigma-X^{5} \Pi,{ }^{5} \Delta-X^{5} \Pi$, and ${ }^{5} \Pi-X^{5} \Pi$ (Hocking et al. 1980; Cheung, Zyrnicki, and Merer 1984; Barnes et al. 1993) electronic transitions A qualitative energy level diagram for a molecule in a ${ }^{5}$ II state is shown in Figure 12. In this schematic it can be seen that CrO is described in a Hund's case(a) basis. Therefore, five spin-orbit components result, each separated by approximately $63 \mathrm{~cm}^{-1}$ in energy. In this work rotational transitions from within all five spin-orbit components were measured. In Figure 12, each rotational transition is split into two by the effect of lambda-doubling. This phenomenon occurs in molecules with non-zero angular momentum ground states $(\Lambda>0)$. The $\pm$ degeneracy of $\Lambda$ is removed through perturbations by other electronic states (primarily $\Sigma$ states). The lambda doublets of each rotational transition are given a parity label based on the Kronig symmetry of the nearest perturbing $\Sigma$ state. In the case of CrO , lambda doubling was resolved in all spin-orbit components (except $\Omega=3$ ). The measured line frequencies for CrO can be found in Appendix F. Since the ground state of CrO is ${ }^{5} \Pi$ all three previously described higher terms $\gamma_{\mathrm{s}}, \theta$, and $\eta$ may be necessary. In the case of CrO only $\eta$ and $\theta$ were included in the Hamiltonian to model the rotational data. Further details on the fitting of the rotational transition data for CrO to a ${ }^{5} \Pi$ Hamiltonian as well as a bonding comparison with CrN can be found in Appendix F .

$$
\text { iii. } \operatorname{FeN}\left(\mathrm{X}^{2} \Delta_{\mathrm{i}}\right)
$$

Iron has the largest interstellar abundance of the transition metals because it is the end product of non-explosive nucleosynthetic processes. Iron containing molecules are of particular interest from the viewpoint of interstellar chemistry (see Appendix H).

Unfortunately no iron containing molecules have been conclusively detected in the interstellar medium to date. Measurements of the pure rotational spectra of iron containing species are necessary in order to find such a molecule. One such species is the FeN radical. FeN was first observed by optical spectroscopy, under jet-cooled conditions (Aiuchi and Shibuya 2000). In this experiment, only the ground state spin-orbit component was identified and assigned a value of $\Omega=5 / 2$. Unfortunately, the ground state term ( $\Lambda$ and $\Sigma$ values) could not be ascertained since additional spin-orbit components had not been observed. Theoretical investigations of FeN (Fieldler and Iwata 1997) revealed four possibilities for the ground state, ${ }^{4} \Pi,{ }^{2} \Delta,{ }^{6} \Sigma$, and ${ }^{4} \Phi$. Immediately, the $\Omega=5 / 2$ ground state assignment eliminates the ${ }^{6} \Sigma$ and ${ }^{4} \Phi$ terms. The measurement of the pure rotational spectrum of FeN revealed very weak rotational transitions belonging to the $\Omega=5 / 2$ sub-level (see Appendix $H$ ). Searches for addition spin-orbit components were unsuccessful, however this was not surprising due to the weak nature of the ground state lines. Since additional spin-orbit components could not be found, theoretical calculations were utilized to assign the ground state of FeN. A high-level $a b$ initio investigation conducted by Hirano favored a ${ }^{2} \Delta$ ground state. The bond lengths of the ${ }^{2} \Delta$ and the ${ }^{4} \Pi$ state were calculated to be $1.5784 \AA$ and $1.5944 \AA$ respectively. The experimental bond length ( $1.5802 \AA$ ) is more comparable to the value for the ${ }^{2} \Delta$ state. Because the experimental bond length is based only on the $\Omega=5 / 2$ spincomponent, the overall bond length of the molecule will shorten if data from the $\Omega=3 / 2$ sub-level is included via Mulliken's relationship (Herzberg 1989). Measured rotational frequencies and spectroscopic constants can be found in Appendix H.
iv. $\operatorname{FeC}\left(\mathrm{X}^{3} \Delta_{\mathrm{i}}\right)$

The pure rotational spectrum of the FeC radical was previously investigated by the Ziurys group (Allen, Pesch, and Ziurys 1996). Unfortunately in this study, only two ( $\Omega=3$ and 2) of the three spin-orbit components were observed for the main isotope ${ }^{56} \mathrm{FeC}$ and one $(\Omega=3)$ for ${ }^{54} \mathrm{FeC}$. The millimeter-wave measurements of the FeN radical led to a reinvestigation of FeC in order to find the missing $\Omega=1$ component. This subsequent reanalysis revealed that the previously assigned $\Omega=3$ spin component of ${ }^{54} \mathrm{FeC}$ was in fact the $\Omega=1$ sub-level of ${ }^{56} \mathrm{FeC}$. The reason for this misassignment can be observed in Appendix H. Unlike in CrO , the three spin-orbit components of FeC are not evenly spaced in frequency. Thus the previous search for the $\Omega=1$ component was concentrated in the wrong frequency region. The uneven splitting is the result of a perturbation of the $\Omega=2$ spin-orbit component by an isoconfigurational ${ }^{1} \Delta$ excited state with $\Omega=2$. The resulting perturbation occurs through the spin-orbit operator, and can be modeled via the spin-spin parameter. The reassignment of the spectrum allowed for a complete case(a) analysis and determination of the molecular parameters the ${ }^{3} \Delta$ state for the first time, including the value of $\lambda$. No higher terms were required or necessary for this molecule. The measured rotational transitions of FeC and a more detailed description of the isoconfigurationalal perturbation can be found in Appendix H.
v. $\operatorname{TiF}\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$

The spectroscopic investigation of TiF is a good illustration of the difficulty associated with assigning the ground state of a molecule. The ground state was first
reported as ${ }^{4} \Sigma$ (Diebner and Kay 1969). Subsequently, a reanalysis resulted in the reassignment of the ground state as ${ }^{2} \Delta$ (Shenyavskaya and Dubov 1985). Most recently a new high-resolution optical study of TiF was conducted and the ground state was reassigned again as ${ }^{4} \Phi$ (Ram et al. 1997). This assignment was made in analogy with $\mathrm{TiH}\left(\mathrm{X}^{4} \Phi\right)$ (Launila and Lindgren 1996) and based on theoretical results (Boldyrev and Simons 1998). However, no measurement of the millimeter-wave spectrum of TiF had been conducted in order to confirm this assignment. The study of TiF is also of interest from the point that $\Phi$ ground states are not very common. Previous to this study, pure rotational transitions of only two other molecules in $\Phi$ states had been recorded, CoH $\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ (Beaton, Evenson, and Brown 1994) and $\mathrm{TiCl}\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)($ Maeda et al. 2001).

The measurement of the pure rotational transitions of TiF confirmed the ${ }^{4} \Phi$ ground state assignment since no additional spin-components beyond those observed in the optical study were found. TiF is a very well behaved case(a) molecule, with a near even splitting of the fine structure components as shown in Appendix I. Measured rotational transition frequencies, spectroscopic constants, and a discussion of bonding trends in the 3d transition metal fluorides are also presented and discussed in Appendix I.

$$
\text { vi. } \operatorname{MnF}\left(\mathrm{X}^{7} \Sigma^{+}\right)
$$

The MnF radical has the largest number of unpaired electron of any molecule studied in this thesis. The six unpaired electrons give rise to seven spin components. Each of these is further complicated by both the $\mathrm{Mn}(\mathrm{I}=5 / 2)$ and $\mathrm{F}(\mathrm{I}=1 / 2)$ nuclei, which have large nuclear magnetic moments. If the spins of the two nuclei are included, the result is 84 total hyperfine components per rotational transition (see Appendix J.

Unfortunately, the relatively small values of the fine and hyperfine parameters resulted in all 84 hyperfine components being compressed into a 100 MHz frequency space. Analysis and assignment of the molecular data was difficult, requiring the aid of a spectral simulation program. Measured rotational transition frequencies, a more detailed analysis of the hyperfine structure, and a further discussion of the bonding in 3 d transition metal fluorides is presented in Appendix J.
4. Molecular Orbital Comparison of $\mathrm{ScO}, \mathrm{TiO}, \mathrm{ScF}$, and TiF

In Appendix I, a plot of bond lengths of the 3d transition metal fluorides and oxides is presented. While the trend in bond length appears to be similar across the 3d row for both the oxide and fluoride species ( $\mathrm{MF} \sim 0.2 \AA$ longer than MO ), deviations at titanium and copper (discussed elsewhere) exist. For titanium, the TiF bond appears to be lengthened. This elongation can be explained by examining qualitative molecular orbital diagrams for the oxide and fluoride species of scandium and titanium, as shown in Figure 13. From ScO to TiO, an extra electron is present in a $1 \delta$ orbital. The addition of this electron should have no effect on the bond order of TiO and because of core contraction between titanium and scandium should result in a shorter TiO bond compared to ScO as observed. In the fluorides, the TiF bond length is elongated compared to ScF . In TiF, the extra electron adds to the $4 \pi$ orbital, which is largely antibonding in character and results in a decrease in the bond order of TiF relative to ScF , lengthening the TiF bond. If the ground state of TiF were either ${ }^{4} \Sigma$ or ${ }^{2} \Delta$ as previously thought, these states could only arise from a $9 \sigma^{1} 1 \delta^{2}$ or a $9 \sigma^{2} 1 \delta^{1}$ configuration, respectively. In both
situations an antibonding orbital is not occupied and an increased TiP bond length relative to ScF would not expected.

Ti

Sc
O
$\mathrm{X}^{2} \Sigma$
$-100$

Sc $X^{\prime}=$
$\mathrm{X}^{3} \Delta$
$-100$
$\begin{array}{ll}3 d- & \frac{1}{4}-4 \pi \\ 4 s-18\end{array}$


Ti

Figure 13. Qualitative Molecular Orbital Diagrams for $\mathrm{ScO}, \mathrm{ScF}, \mathrm{TiO}$, and KiF

From the ground electronic state terms, information about the relative energies of the molecular orbitals can also be obtained. In ScO a single unpaired electron occupies the $9 \sigma$ orbital. In the fluoride counterpart, ScF , an additional electron is present, due to fluorine and it fills the $9 \sigma$ orbital rather than the $1 \delta$. In TiC and RiF an additional electron is present in both species compared to their scandium counterparts. In TiO this
electron occupies the $1 \delta$ orbital unlike in isoelectronic ScF . In TiF, the $9 \sigma$ orbital is no longer full resulting in a $9 \sigma^{1} 1 \delta^{1} 4 \pi^{1}$ configuration not $1 \delta^{1}$, which might be expected from the addition of an extra electron into the MO diagram of ScF . The electron filling schemes of these diatomics may be explained by examining the $9 \sigma-1 \delta$ orbital energy gap between ScF to TiF as indicated by the double arrow. If this energy difference is larger than the spin-pairing energy for the $9 \sigma$ orbital, then the electron configuration observed for ScF results. In TiF, the $9 \sigma-1 \delta$ energy gap must decrease sufficiently such that the $9 \sigma$ pairing energy is greater, resulting in a maximum spin multiplicity. In ScO , there is only one single unpaired electron, therefore it is not possible to make a similar comparison. However, this gap must be small enough in TiO in order for a $9 \sigma^{1} 1 \delta^{1}$ configuration to result. The decrease in the $9 \sigma-1 \delta$ energy difference most likely occurs because the 3d metal atomic orbital decreases in energy relative to the 4 s as one moves from scandium to titanium.

## CHAPTER 6. TRANSITION METAL CYANIDES

## 1. Introduction

Molecules containing a metal atom bonded to the cyanide moiety are encountered in a variety of regions of chemical research (see Appendices $G$ and $K$; Brewster and Ziurys 2002; Grotjahn, Brewster, and Ziurys 2002). These molecules are also of interest from the aspect of their molecular geometry. Three structures are possible for the metal cyanides: linear cyanide (MCN), linear isocyanide (MNC), and t-shaped. However, the geometry of the lowest energy isomer for most metal cyanides is not known. A periodic table of the ground state isomer of the experimentally observed cyanides is shown in
1
$\begin{array}{lllllll}2 & 3 & 4 & 5 & 6 & 7 & 8\end{array}$
$9 \quad 10$
11
12
13


Figure 14. Periodic Table of Experimentally Observed Metal Cyanides.

Figure 14. Both sodium (Van Vaals, Meerts, and Dymanus 1984) and potassium (Törring et al. 1980) cyanide exhibit the t-shaped geometry, a polytopic structure in which the metal ion is coordinated with the $\pi$ cloud of CN . This geometry results when the metal-cyanide bond is almost completely ionic. The remaining species, lithium (van Vaals, Meerts, and Dymanus 1983), the alkaline-earth (Anderson and Ziurys 1994; Steimle, Fletcher, and Steimle 1994), and the group 13 metals (Walker et al. 2001) exhibit the linear isocyanide form as the lower energy isomer (the isomerization energy between InNC InCN is very small). The isocyanide structure is thought to result due to an increase in the covalent bonding character between the metal and CN (Dorigo, Schleyer, and Hobza 1994; Ma, Yamaguchi, and Schaefer 1995). Recently, the first transition metal cyanide, FeNC (Lie and Dagdigian 2001), was detected using laser-induced fluorescence (LIF) spectroscopy. It also exhibited the linear isocyanide structure. Interestingly, up to this point no species with the linear cyanide form as the ground state isomer had yet been observed. However, the extent of the laboratory and theoretical investigations for metal containing cyanides, as shown in Figure 14, is rather limited.

The desire to determine the structure of the remaining transition metal cyanides as well the recent detection of four (half of all metal molecules identified to date) metal cyanides (Ziurys et al. 2002) in the interstellar medium, prompted the Ziurys group to measure pure rotational transitions of these species. The first transition metal cyanide to be observed was $\mathrm{ZnCN}\left({ }^{2} \Sigma^{+}\right)$(Brewster and Ziurys 2002). Measurement of the pure rotational spectrum of zinc cyanide, including five isotopomers led to the unambiguous determination of a linear isocyanide geometry. This work was followed by the detection
of $\mathrm{CuCN}\left({ }^{i} \Sigma^{+}\right)$by pure rotational spectroscopy (Grotjahn, Brewster, and Ziurys 2002). Again several isotopic substitutions indicated that the molecule exhibited the linear cyanide structure. Continuing across the 3 d row, the next species to be investigated was the NiCN radical. Several electronic transitions originating from the $\Omega=5 / 2$ spin-orbit component of the ${ }^{2} \Delta$ ground state were observed using LIF techniques (Kingston, Varberg, and Merer 2002). These authors determined the ground state isomer of the molecule to be the linear cyanide form. This work was followed by measurement of the pure rotational spectra of $\mathrm{NiCN}\left(\mathrm{X}^{2} \Delta_{\mathrm{i}}\right)$ and $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{i}\right)$ in this thesis. The results of these investigations will be summarized in the remaining sections of this chapter.
2. Theory

The general theory applicable to the rotational energy levels in the ground states of the transition metal cyanides $\operatorname{NiCN}\left(X^{2} \Delta_{i}\right)$ and $\operatorname{CoCN}\left(X^{3} \Phi_{i}\right)$ has been described in Chapter 3. Therefore, this section will concentrate on effects arising from the RennerTeller interaction. Linear metal cyanide molecules possess four vibrational modes: a metal-carbon stretch, a carbon-nitrogen stretch and a degenerate bend. The CN stretch lies highest in energy ( $\sim 2000 \mathrm{~cm}^{-1}$ ), followed by the metal carbon stretch $\left(\sim 500 \mathrm{~cm}^{-1}\right)$, and finally the bend, which is lowest $\left(-250-300 \mathrm{~cm}^{-1}\right.$ ) (Kingston, Merer, and Varberg 2002). Because Broida-type ovens are used in the synthesis, the molecules are produced at temperatures $(400-500 \mathrm{~K})$ sufficient to populate the rotational energy levels of the bending vibrational mode (and the metal-carbon stretch). Therefore, rotational transitions within the energy levels of the bending mode may be observed. In the case of ${ }^{2} \Sigma$ or ${ }^{1} \Sigma$ molecules such as ZnCN or CuCN , the rotational spectra of the bending vibrational
modes are subject to a phenomenon known as l-type doubling. The effect is the result of the coupling of the rotational angular momentum to the vibrational motion, and removes


Figure 15. Qualitative Vibrational Energy Level Diagram of a $\Sigma$ Molecule.
the degeneracy of the bending mode (Townes and Schawlow 1975). A qualitative energy level diagram showing this effect is displayed in Figure 15. Here $\left(v_{1} v_{2} v_{3}\right)$ label the metalcarbon stretch, the bend, and the carbon-nitrogen stretch respectively. The $v_{2}=1$ energy level is split into two levels by $l$-type doubling, thus rotational transitions arising form the $v_{2}=1$ mode appear as doublets. Symmetry labels for these levels arise from the value of
the $l$ quantum number. This effect has been observed in many linear triatomic molecules, for example MgOH and AlNC (Apponi, Anderson, and Ziurys 1999; Robinson, Apponi, and Ziurys 1997). Energy level expressions that explicitly model the l-type doubling splitting in the rotational transitions of each bending mode have been developed up to at least $\mathrm{v}_{2}=4$. (Presunka and Coxon 1993; Yamada, Birss, and Aliev 1985; Maki and Lide 1967).

The ground states of $\operatorname{NiCN}\left(\mathrm{X}^{2} \Delta_{i}\right)$ and $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{i}\right)$ have non-zero values of $\Lambda$. The resulting orbital angular momentum can couple with the vibrational angular momentum to form vibronic states ( $\Lambda+l=\mathrm{K}$ ), labeled by K . This coupling, known as


Figure 16. Qualitative Vibronic Energy Level Diagram for a ${ }^{2} \Delta$ Molecule.
the Renner-Teller effect splits the energy levels of the bending mode into vibronic components (Jungen and Merer 1976; Brown and Jørgenson 1983). Figure 16 shows the splitting of the bending vibronic levels of a molecule in $a^{2} \Delta$ state by this effect. The $v_{2}$ $=1$ mode is now split into three and the $\mathrm{v}_{2}=2$ into five components each. The additional vibronic components as well as the uneven energy level separation (Peric and Peyerimhoff 2002) make identification of the rotational transitions of the vibronic components more difficult. The theory of the Renner effect for $\Delta$ and $\Phi$ states has not been developed in as great of detail as for $\Pi$ states, because studies of linear triatomic molecules in $\Delta$ or $\Pi$ states are extremely limited. Unlike for $l$-type doubling, a global energy level expression does not exist for the rotational transitions in the vibronic energy levels of molecules in these states. Thus, each vibronic coupling must be modeled using effective parameters in a case(c) basis (see Appendices G and $K$ ).

As mentioned before, rotational transitions originating in the energy levels of the metal-carbon stretch may be observed. In the case NiCN , the energies of the first quantum of the stretch and the second quantum of the bend are similar. In this case, the bending vibronic component with the same symmetry as the first quantum of the stretch (same as the ground state) will perturb one another separating each other in energy and partially mixing the rotational constants of each state. This effect was experimentally observed to be particularly large in NiCN (Kingston, Merer, and Varberg 2002) and is illustrated in the energy level diagram of NiCN in Appendix G .

## 3. Results and Analysis

The detailed spectroscopic results of the millimeter-wave observations of NiCN $\left(\mathrm{X}^{2} \Delta_{i}\right)$ and $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{i}\right)$ can be found in Appendices $G$ and K . For NiCN, rotational transitions were recorded for five isotopomers, including transitions in the $\Omega=3 / 2$ spinorbit component and several vibronic components for the first time. The rotational spectra indicated that the molecule exhibited the linear cyanide geometry. Representative lab and stick spectra as well as measured rotational transitions and spectroscopic constants can also be found in Appendix G. CoCN was detected for the first time spectroscopically by the millimeter-wave measurements in this thesis. From the pure rotational transitions of the isotopomers, ${ }^{59} \mathrm{CoCN}$ and ${ }^{59} \mathrm{Co}^{13} \mathrm{CN}$, the molecule was determined to have the linear cyanide structure. Hyperfine splittings due to the ${ }^{59} \mathrm{Co}(\mathrm{I}=$ 7/2) nucleus were observed for both isotopomers. Representative laboratory and stick spectra, spectroscopic constants and measured rotational transitions can be found in Appendix K. In both cases, these molecules are the first examples exhibiting the effects of Renner-Teller coupling on the rotational transitions in the bending mode of species in $\Delta$ and $\Phi$ states.

The measured rotational transitions for NiCN and CoCN were fit using the Hamiltonians in Chapter 3. Explicit forms can be found in Appendices $\mathbf{G}$ and $\mathbb{K}$.

## 4. Discussion

i. Structure

The structure of the transition metal cyanides have been determined using several methods. The first is the $\mathrm{r}_{0}$ structure, in which the moments of inertia of the isotopomers of a particular cyanide are fit to the following equation (Gordy and Cook 1984):

$$
\begin{equation*}
\mathrm{I}_{0}=1 / \mathrm{M}\left[\mathrm{~m}_{\mathrm{M}} \mathrm{~m}_{\mathrm{C}} \mathrm{r}_{\mathrm{MC}}^{2}+\mathrm{m}_{\mathrm{C}} \mathrm{~m}_{\mathrm{N}} \mathrm{r}_{\mathrm{CN}}^{2}+\mathrm{m}_{\mathrm{M}} \mathrm{~m}_{\mathrm{N}}\left(\mathrm{r}_{\mathrm{MC}}+\mathrm{r}_{\mathrm{CN}}\right)^{2}\right] \tag{6.1}
\end{equation*}
$$

where $\mathrm{I}_{0}$ is the moment of inertia in the ground vibrational state, M is the total mass of the molecule, $\mathrm{m}_{\mathrm{i}}$ are the masses of the individual atoms, and $\mathrm{r}_{\mathrm{ij}}$ are the bond lengths. Small zero point contributions may result in anomalies in the $r_{0}$ structure. In order to minimize these effects, a substitution structure is determined. This method employs Kraitchman's equations (Gordy and Cook 1984),

$$
\begin{equation*}
|z|=\left[\frac{1}{\mu}\left(I_{x}^{1}-I_{x}\right)\right]^{1 / 2} ; \mu=M \Delta m / M+\Delta m ; \Delta m=m_{\text {sub }}-m_{\text {parent }} \tag{6.2}
\end{equation*}
$$

where the prime denotes the substituted atom and $\Delta \mathrm{m}$ is the mass difference in the isotopic substitution, and the center of mass condition in order to determine a structure closer to the equilibrium value. The final method is the $r_{m}^{(1)}$ method developed by Watson, in an effort to further remove zero-point contamination. Here the moments of inertia are fit to (Watson, Roytburg, and Ulrich 1999)

$$
\begin{equation*}
I_{o}=I_{m}+c \sqrt{I_{m}} \tag{6.3}
\end{equation*}
$$

where $I_{m}$ is the rigid mass dependent moment of inertia and c is a constant. This method and the substitution structure require moments of inertia from at least three isotopomers.

Table 10 contains the bond lengths parameters determined for the transition metal cyanides by the methods previously described.

Table 10. Bond lengths for Transition Metal Cyanides.

|  |  | $r_{M-C}(\AA)$ | $r_{C N}(\AA)$ |
| :---: | :---: | :---: | :---: |
| CoCN | $\mathrm{r}_{0(\Omega=4)}$ | $1.8827(7)$ | $1.1313(10)$ |
|  |  |  |  |
| NiCN | $\mathrm{r}_{0}$ | $1.8283(6)$ | $1.1578(8)$ |
|  | $\mathrm{r}_{0(\Omega=5 / 2)}$ | $1.8293(1)$ | $1.1590(2)$ |
|  | $\mathrm{r}_{\mathrm{s}(\Omega=5 / 2)}$ | 1.8292 | 1.1534 |
|  | $\mathrm{r}_{\mathrm{m}}{ }^{(1)}(\Omega=5 / 2)$ | $1.8263(9)$ | $1.152(1)$ |
|  |  |  |  |
| CuCN | $\mathrm{r}_{0}$ | $1.83231(7)$ | $1.1576(1)$ |
|  | $\mathrm{r}_{\mathrm{s}}$ | $1.83284(4)$ | $1.15669(3)$ |
|  | $\mathrm{r}_{\mathrm{m}}{ }^{(1)}$ | 1.8358 | 1.1573 |
|  |  |  |  |
| ZnCN | $\mathrm{r}_{0}$ | 1.9545 | 1.1464 |
|  | $\mathrm{r}_{\mathrm{s}}$ | 1.9525 | 1.1434 |
|  | $\mathrm{r}_{\mathrm{m}}{ }^{(1)}$ | 1.9496 | 1.1417 |

A discussion of the bond lengths can be found in Appendices $G$ and $K$.

## ii. Bonding

The preference for the 3d transition metals to form cyanides rather than isocyanides may be explained by examining a qualitative molecular orbital diagram for CN as shown in Figure 17. Because the atomic orbitals of nitrogen are slightly lower in energy than those of carbon, the bonding molecular orbitals are slightly more nitrogen in character. Therefore, when the metal atom bonds to CN it would be expected to attach to the nitrogen atom, which is the case for lithium, the alkaline-earth, and the group 13 metal cyanides. However, the transition metals possess nearly full d-orbitals. These electron rich metals may prefer to bond to the carbon side of the cyanide because of back donation of d-electron density into the $\pi^{*}$ orbital of CN , which has a greater carbon


Figure 17. Qualitative Molecular Orbital Diagram for CN.
character. A comparison of the CN bond lengths for the transition metal cyanides and isocyanides would determine if this hypothesis is correct. However, these parameters are not yet known for the higher energy isocyanide isomers.

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## APPENDIX A

## LABORATORY DETECTION OF THE MgNH ${ }_{2}$ RADICAL ( $\mathrm{X}^{2} \mathrm{~A}_{1}$ )

P. M. Sheridan and L. M. Ziurys, Astrophys. J. Letters 540, L61 - L64 (2000).

# LABORATORY DETECTION OF THE MgNH RADICAL $\left(\bar{F}^{2} A_{1}\right)$ <br> <br> P. M. Sherdanan and L. M. Zuurys <br> <br> P. M. Sherdanan and L. M. Zuurys <br>  <br> Received 2000 March 22; acceqped 2000 Jugi 14: pwolished 2000 Augass $2 l$ 

ABSTRACT
The $\mathrm{MgNH}_{2}$ radical has been detected in the laboratory for the frrst tirne in its $\dot{X}^{2} \mathcal{A}_{1}$ ground state using techniques of millimerer-wave spectroscopy. This shori-lived species was created using Broida oven methods. Muliple $K_{0}$ asymmetry components were recorded for $\mathrm{MgNH}_{2}$ in 12 rotational transitions in the frequancy range $129-527 \mathrm{GH} 2$ and spin -rotation splittings were resolved in every component. A total of 251 separate lines were measured. An intensive search for a possible inversion state in $\mathrm{MgNH}_{2}$ was also conducted but proved negative. This data set has been modeled with an $S$-reduced Hiarniltonian and very accurate rotational, centrifugal distortion, and spin-rotation parameters have been determined for msgnesium amide. This study strongly suggess thas the radical is planar with $C_{25}$ symmetry, although small bariers to planarity cannot be ruled out. MgNH , could be produced in interstellar/circumstellar gas from the association reaction of $\mathrm{Mg}^{*}+\mathrm{NH}_{3}$, as predicted by theory.
Subject headings: circurnstellar matter - ISM: molecules - line: identification - methods: laboratory molecular data

## 1. INTRODUCTION

Although magnesiurn has a cosmic abundance comparable to that of silicon, namely, $\mathrm{Mg} / \mathrm{H} \sim 3 \times 10^{-3}$, only two inter. stellar molecules bave been found to date that contain this element. These species are MgNC (Kawaguchi et al. 1993) and MgCN (Ziurys ef al. 1995). Both have been detected toward the late-type carbon star IRC +10216 , and mone recemlly, MgNC has been observed Loward CRL 2688 and CRL 618 (Ziurys, Highberger, \& Savage 2000). Given the wide range of silicon-bearing molecules that have been observed in circumstellar envelopes ( $\mathrm{SiO}, \mathrm{SiS}, \mathrm{SiC}_{2}, \mathrm{SiC}, \mathrm{SiC}_{s}$, eici; e.g., Cermicharo, Guélin, \& Kahane 2000), it is surprising that more Mgcontaining species have not been detected. Again, one prohibiting factor has been the lack of accurate rest frequencies for such compounds. Considerably more silicon-bearing species have been studied in the laboratory, such as $\mathrm{SiC}_{3}, \mathrm{SiC}_{3}$, and $\mathrm{SiC}_{n}$ (e.g. McCarthy et $\mathfrak{\mathrm { al } . 2 0 0 0 \text { ). Hence, in this case, there } { } ^ { \text { 2 } } \text { . }}$ are a greater number of possibilities for inierstellar and circumstellar identifications.
In a recent chemical model of IRC +10216 , Petrie (1996) suggested that radiative association reactions of metal ions and neutral molecules could lead to metal-containing species in this object. In fact, some experimental worls indicates that the reaction

$$
\begin{equation*}
\mathrm{Na}^{+}+\mathrm{NH}_{2} \rightarrow \mathrm{NaNH}_{3}^{+}+\mathrm{hg} \tag{1}
\end{equation*}
$$

may be reasonably fast at interstellar temperatures. The extrapolated rate constant at 20 K is extimated by Petrie to be $\mathrm{s} \sim 10^{-10} \mathrm{~cm}^{3} \mathrm{~s}^{-1}$, which is about an order of magnitude less than the Langevin rate. Subsequent dissociative electron recombination of the $\mathrm{NaNH}_{3}^{+}$complex produces $\mathrm{NaNH}_{2}$, which Petrie concludes is a good candidate for interstellar detection. Moreoves, this author has examined the analogous reactions leading to $\mathrm{MgNH}_{2}$ and $\mathrm{ANNH}_{3}$, which be suggests are comparably efficient. Since the binding energy of the MgNHH complex is higher than the sodium analog (Bauschlicher \& Partridge 1991), Petrie conjectures that $\mathrm{MgNH}_{2}$ might be an even better candidate for an interstellar search than NaNH.
As a consequence of these theoretical studies, our group has been measuring the pure rotational spectra of metal amide spe-
cies. We have recorded, for example, the millimeter-wave spectrum of $\mathrm{NaNH}_{2}$ (Xin, Brewster, \& Ziurys 2000), the frrst laboratory detection of this molecule in the gas phase. Interstellar searches for this compound are currently being conducted.

Here we present our measurements of the pure rotational spectrum of the $\mathrm{MgNH}_{2}$ radical in its $X^{2} A_{1}$ ground electronic state. This study is the first laboratory detection of this species. Twelve rotational transitions of the molecule were recorded in the frequency range $129-527 \mathrm{GHz}$, including asymmetry components as high as $K_{e}=7$. Highly accurate spectroscopic constants have subsequently been determined for $\mathrm{MgNH}_{2}$. In this Letter we describe our results.

## 2. EXPERIMENTAL

Spectroscopic measuremerats of $\mathrm{MgNH}_{2}$ were done using one of the millimeter/submillimeter spectrometers of the Ziurys group, described in detail elsewhere (Ziurys et al. 1994). The instrument employs a Gunn oscillator/Schonky diode multiplier combination as the frequency source, a reaction chamber, and an InSb bolometer detector. This system uses teflon lenses and a wire grid to quasi-opucally propagate the radiation through the double-pass reaction cell, which incorporates a Broida-type oven. Frequency modulation of the radiation allows for phasesensitive detection.

Magnesium amide was synthesized in a DC discharge of magnesium vapor, argon, and ammonia gases. The argon and ammonia were added to the reaction cell ogether in a $1: 1$ ratio of about 15 mitor per gas. The magnesivm vapor was produced using the Broida-type oven. A steel plate with an opening slightly smaller than the diameter of the crucible was placed over the oven in order to collimate the magnesium vapor. Argon was incroduced into the cell from underneath the oven, serving as a carrier gas, whilie the ammonia was flowed in over the top of the oven. A DC discharge currem of $650-850 \mathrm{~mA}$ was used at 30 V . A bright, green-colored discharge was observed, arising from atomic emission of magnesium.

No previous experimental data existed for MgNH . Hence, an initial search had to be conducted over a 70 GHz range, which is approximately 6 times the value of the estimated effective rotational constant. This frequency range, covering $460-530 \mathrm{GHz}$, was scanned coninuously in 100 MHzz intervals.

TABLE 1


| $N^{+}-N^{*}$ |  | ${ }_{\sim}^{*}-E_{5}$ | $y^{\prime} \sim 5$ | Pmom |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 5-4........ | 1-1 | 5-4 | 4.5-3.3 | 129529.697 | -0.008 |
|  | $\frac{1}{1}-1$ | $5-4$ | 5.5-4.5 | 129568.588 | 0.010 |
|  | 1-1 | --3 | 4.5-3.5 | 131906.673 | 0.034 |
|  | 1-1 | 4-3 | $5.5-4.5$ | 131986.543 | 0.021 |
| 6-5........ | 1-1 | 6-5 | $5.5-4.5$ | 159432.988 | -0.030 |
|  | 1-1 | 6-5 | 6.5-5.5 | \$55471.705 | -0.027 |
|  | 1-1 | 5-4 | $5.5-4.5$ | 138284.859 | -0.028 |
|  | $1-1$ | $5-4$ | 6.5-5.5 | 158324.558 | -0.023 |
| 9-8....... | 1-1 | 9-8 | $8.5 \leftarrow 7.5$ | 233117.964 | -0.062 |
|  | 1-1 | $9-8$ | 9.5-8.5 | 233156.535 | -0.039 |
|  | 2-2 | $8-7$ | 9.5-8.5 | 235199.672 | 0.114 |
|  | 2-2 | 7-6 | 85-7.5 | 235214.423 | -0.020 |
|  | $0<0$ | 9-3 | 8.5-75 | 235267.037 | -0.003 |
|  | 2-2 | 7-6 | $9.5-8.5$ | 235254.050 | 0.026 |
|  | 0-0 | 9-8 | 9.5-8.9 | 235285.788 | -0.049 |
|  | 1-1 | 8-7 | 8.5-7.5 | 237393.209 | $<0.000$ |
|  | 1-1 | $8-7$ | 9.3-8.5 | 237432.665 | $-0.1003$ |
| 10-9...... | 1-1 | $10 \sim 9$ | $9.5-8.5$ | 259002.845 | -0.012 |
|  | 1-1 | 10-9 | 10.5-9.5 | 259041.445 | 0.076 |
|  | 2-2 | 9-8 | 9.5-8.5 | 261272.533 | -0.056 |
|  | 2-2 | 9-8 | 10.5-93 | 261312.022 | (0.027 |
|  | 2-2 |  | $9.5-8.5$ | 261347.326 | -0.081 |
|  | 0-0 | $10-9$ | 9.5-8.5 | 261356.691 | -0.015 |
|  | 2-2 | $8-7$ | 30.5-9.5 | 261386.849 | - 0.008 |
|  | $0-0$ | $10 * 9$ | 10.5-9.5 | 261395.576 | 0.081 |
|  | 1-1 | 9-8 | 9.5-8.3 | 263751.622 | -0.077 |
|  | 1-1 | 9-8 | 10.5-9.5 | 253791.167 | 0.046 |
| 12-11..... | $1-1$ | 12-11 | $11.5-10.5$ | 310753.521 | -0.099 |
|  | 1-1 | 12-11 | $12.5-11.5$ | 310792.130 | 0.048 |
|  | 2-2 | 11-10 | 11.5-10.5 | 313479.463 | -0.024 |
|  | 2-2 | 11-10 | 12.5-11.5 | 313518.722 | 0.011 |
|  | 0-0 | $12-11$ | 11.5-10.5 | 313545.675 | -0.021 |
|  | 0-0 | 12-11 | 12.5-11.5 | 313584.492 | 0.027 |
|  | 2-2 | 10-9 | 11.5-10.5 | 313608.988 | -0.070 |
|  | 2-2 | 10-9 | 12.5-11.5 | 313648.368 | 0.022 |
|  | 1-1 | $11-10$ | 11.5-10.5 | 316048.287 | -0.082 |
|  | 1-1 | $11-10$ | 12.5-11.5 | 316487.734 | 0.033 |
| 13-12..... | 1-1 | $13-12$ | 12.5-11.5 | 336518.274 | -0.077 |
|  | 1-1 | $13-12$ | 13.5-12.5 | 336656.836 | 0.040 |
|  | 2-2 | $12-11$ | 12.5-11.5 | 339572.649 | 0.002 |
|  | 2-2 | 12-11 | 13.5-12.5 | 339611.841 | 0.032 |
|  | $0-0$ | $13-12$ | 125-11.5 | 339623.100 | 0.017 |
|  | 0-0 | 13-12 | $13.5-12.5$ | 339661.899 | 0,0.5s |
|  | 2-2 | 11-10 | 12.5-11.5 | 339737.470 | 0.002 |
|  | 2-2 | 11-10 | $13.5-125$ | 339776.741 | 0.036 |
|  | 1-1 | 12-11 | 12.5-11.5 | 342785.091 | -0.060 |
|  | 1-1 | 12-11 | $13.5-125$ | 342824.527 | 0.021 |
| 14-13..... | 1-1 | $14-13$ | 13.5-12.5 | 362475.169 | -0.014 |
|  | 1-1 | $14-13$ | 14.5-13.5 | 362513.456 | 0.043 |
|  | 2-2 | 13-12 | 13.5-12.5 | 365658.156 | -0.016 |
|  | 0-0 | 14-13 | 13.5-12.5 | 365687.742 | -0.038 |
|  | $2-2$ | $13-12$ | 14.5-13.5 | 365697.388 | 0.0 .61 |
|  | 0-0 | 14-13 | 14.5-13.5 | 365726.581 | 0.055 |
|  | 2-2 | 12-11 | $13.5-12.5$ | 365864.039 | -0.032 |
|  | 2-2 | $12-11$ | 14.5-13.5 | 365903.280 | 0.0009 |
|  | 1-1 | 13-12 | 13.5-12.5 | 369113.383 | -0.047 |
|  | 1-1 | 13-12 | $14.5-13.5$ | 369152.807 | 0.037 |
| 15-14..... | 1-1 | $15-14$ | 14.5-13.5 | 388323.308 | -0.010 |
|  | 1-1 | $15-14$ | 15.5-14.5 | 388361.975 | . 0.039 |
|  | 2-2 | $14-13$ | 14.5-13.5 | 391735.441 | -0.037 |
|  | 0-0 | $13-14$ | 14.5-13.3 | 391738.824 | -0.006 |
|  | 2-2 | $14-13$ | 13.5-14.5 | 391774.575 | 0.024 |
|  | 0-0 | 15-14 | 15.5-14.5 | 391777.601 | 0.038 |
|  | $2-2$ | $13-12$ | 14.5-13.5 | 391988.697 | -0.018 |
|  | 2-2 | $13-12$ | 15.5-14.9 | 392027.889 | 0.003 |
|  | 1-1 | 14-13 | 14.5-13.5 | 395432.510 | 0.006 |
|  | $1-1$ | 14-13 | 15.55-14.5 | 395471.847 | 0.016 |
| 17-16.... | $1-1$ | 17-16 | 16.5-15.5 | 439992.323 | <0.000 |
|  | $1-1$ | 17-16 | $17.5-16.5$ | 400030.728 | 0.009 |
|  | $0-0$ | 17-16 | $16.5-15.5$ | 4437\%.197 | 0.010 |
|  | 0-0 | 17-16 | 17.5-16.5 | 443834.69\% | 0.004 |
|  | 2-2 | 16-15 | $16.5-15.5$ | 443863.067 | -0.032 |


| $N^{\prime}-\mathrm{A}^{\prime \prime}$ |  |  | $y^{\prime}-f$ | $\$_{\text {demo }}$ | $\mathrm{s}_{\text {ctat }}-{ }^{\text {costa }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 18-17..... | 2-2 | 15-15 | 17.5-16.5 | 443992.188 | 0898 |
|  | 2-2 | 15-14 | $16.5-15.5$ | 444231.476 | 0.006 |
|  | 2-2 | 15-14 | 17.5-16.5 | 444270.608 | -0.001 |
|  | 1-1 | 16-15 | 36.5-15.5 | 489040.351 | -0.028 |
|  | 1-1 | 16-15 | 17.5-16.5 | 448079.702 | 0.018 |
|  | 1-1 | 118-17 | 17.5-16.5 | 465811.523 | 0.014 |
|  | 1-1 | 18-17 | 18.5-17.5 | 465849.949 | -0.047 |
|  | $0-0$ | 18-17 | $17.5-16.5$ | 469800.629 | 0.016 |
|  | - $0-0$ | 18-17 | $18.5-17.5$ | 489839.285 | -0.017 |
|  | 2-2 | 17-16 | $17.5-16.5$ | 469912.317 | 0.070 |
| 19-18..... | 2-2 | 17-16 | 18.5-17.5 | 469951.199 | -0.035 |
|  | 2-2 | 16-15 | 17.5-16.5 | 470349.284 | 0.042 |
|  | 2-2 | 16-15 | 18.5-17.5 | 470388.269 | -0.103 |
|  | 1-1 | $17-16$ | $17.5-16.5$ | 474327.816 | -0.031 |
|  | 1-1 | 17-16 | 18.5-17.5 | 474367.134 | -0.008 |
|  | $1-1$ | 19-18 | 18.5-17.5 | 491620.034 | $<0.000$ |
|  | $1-1$ | 19-18 | $19.5-18.5$ | 491658.388 | -0.025 |
|  | $0-0$ | 19-18 | 18.5-17.5 | 495787.733 | 0.102 |
|  | $\beta-0$ | 19-18 | 19.5-18.5 | 495826.273 | -0.031 |
|  | 2-2 | 18-17 | 18.5-17.5 | 493950841 | $<0.000$ |
| 20-19.... | $2-2$ | 18-17 | 19.5-18.5 | 495989.785 | -0.022 |
|  | 2-2 | 17-16 | 18.5-17.5 | 496464.383 | 0.015 |
|  | 2-2 | 17-16 | $19.5-18.5$ | 496503.481 | -0.012 |
|  | 1-1 | 18-17 | 18.5-17.5 | 300003.453 | 0.019 |
|  | 1-1 | 18-17 | 19.5-18.5 | 500642.704 | -0.027 |
|  | 1-1 | 20-19 | 19.5-18.5 | 517417.008 | -0.004 |
|  | $1-1$ | 20-19 | 20.5-195 | 517855.315 | -0.068 |
|  | 0-9 | 20-19 | 19.5-185 | 521756.320 | -0.004 |
|  | $0-0$ | 20-19 | 20.5-19.5 | \$21794.944 | -0.036 |
|  | $2-2$ | 19-18 | 19S-18.5 | 521978.335 | 0183 |
|  | 2-2 | 19-18 | 20.5-19.5 | 522017.138 | -0.110 |
|  | 2-2 | 18-17 | 19.5-18.5 | \$22576.656 | 0.003 |
|  | 2-2 | 18-17 | 20.5-19.5 | 522615.781 | 0.004 |
|  | 1-1 | 19-18 | 19.5-18.5 | 526886. 469 | -0.831 |
|  | 1-1 | 19-18 | 20.9-19.5 | 526905.752 | -0.026 |

" ${ }^{\circ}$ numis of megaberiz

This intensive initial search enabled the pattern of the spectra to be established and preliminary effective rotational constanks 20 be obtained. Spectral lines from other transitions could then be fairly accurately predicted ( $\pm 50 \mathrm{MH} 1 \mathrm{z}$ ) and therefore considerably namowed the search range. Actual frequency measurements were conducted by fituing Gaussian profiles to features using scans 5 MHz in frequency coverage. For most lines, 2-4 such scans were averaged (an equal number in increasing and decreasing frequency), Below 180 GHz 8-16 scan averages were necessary. Observed line widths were $350-1000 \mathrm{kHz}$ over the range $120-530 \mathrm{GH}$.

## 3. RESULTS

A subset of the transixion frequencies obtained for $\mathrm{MgNH}_{3}$ is given in Table 1. As is the case for any ${ }^{2} A$ electronic state, the quantum numbers labeling the energy levels are $N_{\left(r_{s} f_{k} ; ~\right.} / N$ is the rotational quantum number (case b coupling scheme) and $\mathbb{K}_{0}$ and $\mathbb{K}_{c}$ are the projections of the rotational angular momenturn along the $\overline{6}$ or $\hat{c}$ symmery ases in the prolate and oblate limis ( $\mathbb{K}_{s}+\mathbb{K}_{8}=N$ or $\left.N+1\right) ; J$ accounts for the fupestructure splitings, doublets in this case, where $\hat{J}=\hat{N}+\hat{S}$.
$\mathrm{MgNH}_{2}$ appears to be planar with $\mathrm{C}_{2 \mathrm{r}}$ symmetry, as will be discussed later Hence, the only dipole monent lies along the $\hat{a}$-axis, resulaing in $a$-type $\left(\Delta K_{c}=0, \Delta K_{c}= \pm 1\right)$ transitions. Since the value of $K_{\text {d }}$ does not change, this quanum number can be used to label the asymmetry components present in each $N \rightarrow N+1$ transition. Asymmetry splits many $K_{\infty} \neq 0$ com-


Fals. 1.-Stick specerume showing the sypical progessian of the $K_{0}$ ssymsurectry conuparents in $\mathrm{MgNH}_{\mathrm{y}}$ within the $N=18 \rightarrow 19$ rotational transition. The relaive innemsities result partly from protom spin statistics. The $\mathbb{K}_{\mathrm{s}}=1$ ssymuery doubless are split the widest in ibe palkem. whille the $\mathbb{R}_{\mathrm{o}}=2$ limes have modorrat separation. The rest of the $\mathcal{K}_{\alpha}$ components are collapsed or nearly collupsed into single fectures. (Spin-rotation spliecings are too small to be shown on this scate.)
ponents into doublets. The patem of the $K_{e}$ "doublets" depends on the geometry and degree of asymmetry in the molecule. Another consequence of $\mathrm{C}_{2}$ symmetry is intensity variation due to nuclear spin statistics. The protons can be exchanged in $\mathrm{MgNH}_{2}$ by a $\mathrm{C}_{2 \mathrm{z}}$ rotation. Since the total wave function of the molecule must be antisymnetric on exchange of fermions, odid $K_{0}$ components are favored statistically over even $K_{a}$ lines by a facior of $3: 1$ (see Gordy \& Cook 1984), not including any Bolzzmann factor
The typical spectral pattern resulting from these effects is illustrated in Figure 1. This figure is a sick diagram showing the frequencies and relative intensities of $K_{\mathrm{a}}$ componenss of the $N=18 \rightarrow 19$ rotational transition near 496 GHz As the diagramo illustrates, the $K_{c}=1$ doublets are splii apart from each other by $\rightarrow 9 \mathrm{GHz}$ The nondegenerate $K_{s}=0$ transitions lie near the center of the pattern. As is characteristic of high $N$-values of $\mathrm{MgNH}_{2}$, the $\mathrm{K}_{\mathrm{e}}=2$ doublets lie higher in frequency relative to the $K_{0}=0$ transitions and are split by only $\sim 500 \mathrm{MHz}$. In contrast, the $K_{0}=3,4,5$, and 7 lines occirr at lower frequencies with respect to the $K_{o}=0$ line, and the asymmetry separation steadily decreases so that it cannot be resolved at $K_{0} \geq 4$. Spinrotation inseractions additionally split every $K$. component into doublets separated by about $30-40 \mathrm{MHz}$, which is 100 small to be shown on this plot. Finally, an approximate $3: 1$ imtensity pattern for $K_{\text {, odd }}$, $K_{\text {, }}$ even is apparent in this diagram, which is calculated for a temperaure near 500 K
Assignment of the individual $K_{\text {a }}$ compponents was not trivial. It could be accomplished only after scanning - $6 B$ in frequency space ( $\sim 70 \mathrm{GHz}$ ). Harmonic relationships could then be eslablished among the componens. The incensity patem and spin-rotation splitings also aided in identifying harmonically related lines, and $K_{c}$ quantum number assignments were established by exitrapolating to the symmetric top limit. Verifcation of assiguments was accomplished by obeaining a reasonable fit to the data using a ${ }^{2} A$ Hamilonian.
Usually components corresponding to $K_{0}=0-5$ and $K_{0}=7$ were recorded per rotational transition. The complese


Fga. 2.-Actusal spectrum of 自 section of the $N=18 \rightarrow 19$ transixican ar MgNH, $\left(\dot{F}^{2} A_{3}\right)$ showing the $A_{0}=0,2$ and 3 componemss. which are labeled
 The doubless present in esch indicaled mansition arise frosn spin-routhies ayeverctions. One $\mathbb{F}_{0}=0$ finc-structure componemt is blended with a $\mathcal{K}_{\mathrm{a}}=3$ line. This specoums covers 1.2 GHz and is a composias of 12100 MHz scans, each approximasely 1 mizuse in darasion.
set of $X_{0}$ components was used to deternine spectroscopic consingis. However, only the lower $\mathbb{K}_{g}$ components are relevant to astronomy, and only these are included inTable 1.

Figure 2 shows a typical laboratory spectrum obtained for MgNH. presenting a section of the $N=18 \rightarrow 19$ transition containing the $K_{o}=0,2$, and 3 components. The $\mathbb{K}_{e}=2$ ssymmetry doublets are separated by more than 500 MHz , and ach transition is splat again by about 39 MHz as a result of spin-rotation interactions. In contrast, asymmetry doubling is much smaller in the $K_{a}=3$ lines $(\sim 5-6 \mathrm{MHz})$, and the spinrotation coupling is then the larger interaction. The $K_{0}=0$ transitions are split only by fine structure, and one component is blended with a $K_{o}=3$ line. The features marked by asterisks are due to vibrationally excited states.

## 4. ANALYSIS AND DISCUSSION

The data ser was modeled with a Hamilronian consisting of rotational, cenorifugal distortion, and spin-rotation terms:

$$
\begin{equation*}
\hat{H}_{\mathrm{cry}}=\tilde{H}_{\mathrm{sad}}+\hat{H}_{c d}+\hat{H}_{\mathrm{sr}} \tag{2}
\end{equation*}
$$

A modified fom of the S-reduced Hamitonian of Watson (1977) was used for the first two expressions, the second which incorporates several finh-order centrifugad distorion corrections. The spin-rotation Hamiltonian is a tensor term of the fonm

$$
\begin{equation*}
H_{s s}=\frac{1}{2} \sum_{m A} \epsilon_{\infty A}\left(N_{a} S_{\theta}+S_{\theta} N_{o}\right) \tag{3}
\end{equation*}
$$

Fot species with $C_{2 r}$ symmery, however, all off-diagonal elements are zero. Spectroscopic parameters were obtained by fitting all 251 meas ured lines with the least-squares fiting program SPFIT developed by $\mathrm{H} . \mathrm{M}$. Pickett. in addition to the rotational and spin-rotation constants, eight centrifugal distor-
tion parameters were needed to obtain a reasonable fil These constants are listed in Table 2. The mas of the fut was 51 kHz , well within the mensurement uncerainty of $\pm 100$ k ${ }^{2} \mathrm{~Hz}$
$\mathrm{MgNH}_{2}$ appears to be a planar molecule with $\mathrm{C}_{2}$ symmetry, at least to a good approximation. (A low barrier to planarity is difficult to rigorously exclude). Evidence for planarity is the small, positive inertial defect of $\Delta=0.078$ found for this radical, which did not change sign on deuterium substitution (Sheridan \& Ziurys 2000). Furthermore, the spin-rotation splitting was readily reproduced without use of off-diagonal terms necessary for $C_{3}$ symmerry. The species also does not appear to be undergoing inversion. In the 70 GHz searched, there was no evidence of ospectum arising from an upper inversion state, which would easily be recognized as a "mirnor image" of the lower inversion state with opposite spin statistics. The additional lines that were found with the characteristic spinnotation splitting of MgNH , were typically much weaker, they can be ateributed io $g_{4}$ or $v_{6}$ excited vibrational states.
Planarity indicates an ionic bonding scheme, as has been found for $\mathrm{CaNH}_{2}$ (Mar et al. 1995; Brewster \& Ziurys 2000) and $\mathrm{SrNH}_{2}$ (Brazier \& Bernath 2000; Thompsen, Sheridan, \& Ziurys 2000). In this case the strucure of the amide is $\mathrm{M}^{+} \mathrm{NH}_{2}$. However, the relative magnitudes of the spin-roxation constants change in $\mathrm{MgNH}_{2}$ relative to its calciuma and strontium analogs. As discussed by Curl (1965), this implies a change in the $g$ tensor and therefore the orientation of the
table 2
SPECTROSCOPIC CONSTARTS FOR. M\&NH $\left(\dot{x}^{2} A_{1}\right)^{\circ}$

| Prameter | Value |
| :---: | :---: |
| A ............. | 378525 (42) |
| 8 | 13314.7718 (47) |
| C ............. | 12839.1166 (46) |
|  | 0.0215749 (28) |
| $\mathcal{D}_{\text {aty }} \ldots \ldots . . . . . .$. | 1.86805 (29) |
| $d_{1} \ldots \ldots . . . . . . .$. | -0.0008811 (37) |
| $\varepsilon_{2} \ldots . . . . . . . . .$. | -0.0002076 (17) |
| $H_{\text {asm }}$............ | -0.001184 (11) |
| $H_{\text {mx }} \ldots \ldots . . . . . . .$. | 2.886 (32) $=10^{-5}$ |
| $P_{s m}$ | $-8.992(30)=10^{-1}$ |
| $P_{\text {mex }} \ldots \ldots . . . . .$. | 3.60 (14) $\times 10^{-8}$ |
| $\mathrm{f}_{8}$............. | 24.49 (33) |
|  | 39.743 (90) |
|  | 37.923 (88) |
| mms of fill..... | 0.051 |

orbitals of the unpaired electron relative to the molecule-fixed mads. Consequenaly, $\mathrm{MgNH}_{2}$ differs from $\mathrm{SrNH}_{2}$ and $\mathrm{CaNH} H_{2}$ in its electronic structure, but not enough to drastically alter its geometry.

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## APPENDIX B

ROTATIONAL SPECTROSCOPY OF THE SrNH $H_{2}$ AND SIND ${ }_{2}$ RADICALS $\left(\mathrm{X}^{2} \mathrm{~A}_{1}\right)$
J. M. Thompsen, P. M. Sheridan, and L. M. Ziurys, Chem. Phys. Lett. 330, 373-382 (2000).

# Rotational spectroscopy of the $\mathrm{SrNH}_{2}$ and $\mathrm{SrND}_{2}$ radicals ( $\tilde{\mathrm{X}}^{2} \mathrm{~A}_{1}$ ) 

\author{
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}

## Abstract

The pure rotational spectrum of the $\mathrm{Sr}_{\mathrm{N}} \mathrm{H}_{2}$ radical in its $\overline{\mathrm{X}}^{2} \mathrm{~A}_{1}$ state has been recorded using sub-millimeter direct absorption techniques in the range $225-540 \mathrm{GHz}$. Measurements of $\mathrm{SiND}_{2}$ have also been conducted. Both molecules were produced by the reaction of metal vapor and $\mathrm{NH}_{3}$ or $\mathrm{ND}_{3}$. Fourteen and fifteen rotational eransitions were recorded for $\mathrm{SrNH}_{2}$ and $\mathrm{SrND}_{2}$, respectively. Asymmetry doublets for $K_{\rho}=0$ through 5 or 6 , as well as fine structure splittings, were observed in every transition. From these data, spectroscopic constants have been determined, as well as an $7_{0}$-structure. This study provides additional evidence that $\mathrm{SrNH}_{2}$ is planar with ionic bonding. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Imtroduction

A prime way of probing the metal-ligand bond is through using gas-phase spectroscopy of small, metal-containing molecules. Recent classes of species that have been studied to examine such bonding schemes include $\mathrm{MOH}, \mathrm{MX}, \mathrm{MCH}_{3}$, and $\mathrm{MNH}_{2}$, using both optical and millimeter-wave (mm-wave) techniques e.g., [1-5]. In addition to the alkali metals, such investigations have focused heavily on the alkaline-earth elements $\mathrm{Mg}, \mathrm{Ca}, \mathrm{Sr}$, and Ba. (See Bernath for a review [6].) Analysis of the spectra of such radicals has yielded interesting information about their electronic properties and structure.

The strontium analogs of these molecules provide an important link for understanding chemical irends in the alkaline-earth series. Prior spectroscopic studies of the isovalent alkaline-earth monohydroxide, monomethyl and halide species have shown that strontium compounds have similar properies 10 their calcium and barium counterparts $[6-8]$ and exhibit primarily ionic behavior. For example, it has been shown that $\mathrm{CaOH}, \mathrm{BaOH}$, and SrOH are tightly bound species with a linear geometry and an $\mathrm{M}^{+} \mathrm{OH}^{-}$ structure [7]. It is only MgOH that does not follow these rrends, being quasi-linear, and therefore having more covalent character to the metal-OH bond 19].

Another strontium molecule of interest is $\mathrm{SrNH}_{2}$, which was first observed by Wormsbecher et al. [10]. These authors detected chemiluminescence arising from the reaction of Sr metal vapor with hydrazine or ammonia. They observed three

[^0]Table :
Selected fransition frequencies of $\mathrm{SrNH}_{2}$ and $\mathrm{SrND}_{7}\left(\overline{\mathrm{X}}^{2} A_{1}\right)^{3}$

| $N^{\prime}\left(\mathbb{S}_{\mathrm{a}}^{\prime} \cdot \mathcal{E}^{\prime}\right)^{\prime \prime}$ | $N^{*}\left(K_{0}^{m} \cdot K_{r}^{m}\right]^{\prime \prime}$ | $\mathrm{SrNH}_{2}$ |  | $\mathrm{Sr}_{5} \mathrm{ND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $v_{\text {dos }}$ | $v_{\text {case }}-v_{\text {a }}$ | $v_{\text {de }}$ | $v_{\text {des }}-v_{\text {ate }}$ |
| 17(1,17) 16.5 | 16(1,18) 15.5 | 227325.349 | -0.031 |  |  |
| 1761,17) 17.5 | 16(1,16) 16.5 | 227407.200 | 0.011 |  |  |
| $17(3,15)$ 16.5 | $16(3,14) 15.5$ | 228063.034 | 0.021 |  |  |
| 17(3,14) 16.5 | 16(3,13) 15.5 | 228063.034 | -0.028 |  |  |
| 17(3,14) 17.5 | $16(3,13) 16.5$ | 228135.067 | 0.089 |  |  |
| $17(3,15) 17.5$ | 16(3.14) 16.5 | 228135.067 | 0.136 |  |  |
| 17(1,16) 16.5 | 16(1,15) 15.9 | 229549.898 | 0.071 |  |  |
| 171,16) 17.5 | 16(1,15) 16.5 | 229616.847 | -0.031 |  |  |
| 28(5,23) 27.5 | 27(5,22) 26.5 | 373871.796 | -0.087 |  |  |
| 28(5,24) 27.5 | 27(5,23) 26.5 | 373871.796 | -0.087 |  |  |
| 28(5,23) 28.5 | 27(5,22) 27.5 | 373943.386 | -0.084 |  |  |
| 28(5,24) 28.5 | 27(5,23) 27.5 | 373943.386 | -0.084 |  |  |
| 28(1,28) 27.5 | 27(1,27) 26.5 | 374098.585 | 0.073 |  |  |
| 28(1.28) 28.5 | 27(1.27) 27.5 | 374180.918 | -0.009 |  |  |
| 28(4,25) 27.5 | 27(4,24) 26.5 | 374735.178 | 0.142 |  |  |
| 28(4,24) 27.5 | 27(4,23) 26.5 | 374735.178 | 0.141 |  |  |
| 28(4.25) 28.5 | 27(4,24) 27.5 | 374807.838 | 0.153 |  |  |
| 28(4,24) 28.5 | 27(4,23) 27.5 | 374807.838 | 0.153 |  |  |
| $28(3,26) 27.5$ | 27(3,25) 26.5 | 375 339,976 | -0.034 |  |  |
| 28(3,25) 27.5 | 27(3,24) 26.5 | 375340.381 | -0.229 |  |  |
| 28(3,26) 28.5 | 27(3,25) 27.5 | 375413.417 | -0.014 |  |  |
| 28(3,25) 28.5 | 27(3,24) 27.5 | 375413.834 | -0.184 |  |  |
| 28(2,27) 27.5 | 27(2,20) 26.5 | 375706.080 | 0.138 |  |  |
| 28(2,27) 28.5 | $27(2,26) 27.5$ | 375780.402 | 0.003 |  |  |
| 28(2,26) 27.5 | 27(2,25) 26.5 | 375818.323 | 0.056 |  |  |
| $28(2,26) 28.5$ | 27(2,25) 27.5 | 375891.258 | 0.013 |  |  |
| 28(0,28) 27.5 | 27(0,27) 26.5 | 375903.139 | -0.059 |  |  |
| 280,28) 28.5 | 27(0,27) 27.5 | 375979.245 | -0.130 |  |  |
| 28(1,27) 27.5 | 27(1.26) 26.5 | 277740.326 | 0.065 |  |  |
| 28(1,27) 28.5 | 27(1,26) 27.5 | 377807.690 | -0.040 |  |  |
| 33(6,27) 32.5 | 32(6,26) 31.5 |  |  | 374956.416 | -0.019 |
| 33(6,28) 32.5 | 32(6,27) 31.5 |  |  | 374956.416 | -0.019 |
| 33(6,27) 33.5 | 32(6,26) 32.5 |  |  | 375019.356 | -0.006 |
| 33(6,28) 33.5 | 32(6,27) 32.5 |  |  | 375019.356 | -0.006 |
| 33(1.33) 32.5 | 32(1.32) 31.5 | 440658.322 | 0.087 |  |  |
| 33(1,33) 33.5 | 32(1.32) 32.5 | 440740.880 | 0.066 |  |  |
| 34(4,30) 32.5 | 32(4.29) 31.5 | 441434.099 | -0.083 | 376302.617 | 0.058 |
| 33(4,29) 32.5 | 32(4,28) 31.5 | 441434.099 | -0.088 | 376302.617 | -0.086 |
| 33(4.30) 33.5 | 32(4.29) 32.5 | 441507.074 | -0.127 | 376366.004 | 0.087 |
| 33(4,29) 33.5 | 32(4,28) 32.5 | 441507.074 | -0.132 | 376366.004 | -0.054 |
| 33(3,31) 32.5 | 32(3,30) 31.5 | 442141.702 | -0.037 |  |  |
| 33(3,30) 32.5 | 32(3.29) 31.5 | 442143.149 | 0.045 |  |  |
| 34(3,31) 33.5 | 32(3,30) 32.5 | 442215.265 | -0.061 |  |  |
| 33(3,30) 33.5 | 32(3,29) 32.5 | 442236.6\% | 0.032 |  |  |
| 33(2.32) 32.5 | 32(2,31) 31.9 | 442554.612 | 0.053 |  |  |
| 33(2,32) 33.5 | 32(2,31) 32.5 | 442629.225 | 0.011 |  |  |
| 33(0.33) 32.5 | 32(0.32) 31.5 | 442736.271 | -0.046 |  |  |
| 33(2,31) 32.5 | 32(2,30) 31.5 | 442737.826 | 0.042 | 377507.401 | -0.030 |
| 33(2,31) 31.5 | 32(2,30) 32.5 | 442810.399 | 0.008 | 377657.436 | -0.094 |
| 33(0.33) 33.5 | 32(0,32) 32.5 | 442812.892 | -0.172 |  |  |
| 33(1,32) 32.5 | 32(1,31) 31.5 | 44936.027 | 0.054 |  |  |



| $N^{\prime}\left(K_{n}^{\prime}, E_{c}^{\prime}\right)^{\prime \prime}$ |  | $\mathrm{Sr}_{\mathbf{N H}}^{2}$ |  | $\mathrm{SrND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $v_{\text {com }}$ | $v_{\text {ota }}-v_{\text {a }}$ | $\square_{\text {ofo }}$ | $v_{\text {dian }}-v_{\text {ame }}$ |
| 40(5,35) 39.5 | 39(5,34) 38.5 |  |  | 455128.800 | 0.059 |
| 40(5,36) 39.5 | 39(5,35) 38.5 |  |  | 455128.800 | 0.063 |
| $40(5,35) 40.5$ | 39(5,34) 39.5 |  |  | 455191.965 | -0.009 |
| 40(5,36) 40.5 | 39(5,35) 39.5 |  |  | 455191.965 | -0.006 |
| 4044303) 39.5 | $39(4,35) 38.5$ | 534622.704 | 0.035 | 455846.180 | -0.210 |
| 40(4,37) 39.5 | 39(4,36) 38.5 | 53462.704 | 0.053 | 455846.180 | 0.346 |
| $40(4,36)$ \$0.5 | 39(4,39) 39.5 | 536695.931 | 0.039 | 455909.407 | -0.263 |
| $40(4,37) 40.5$ | 39(4,36) 39.5 | 534695.931 | 0.058 | 455909.407 | 0.285 |
| 40(3,38) 39.5 | $39(3,37) 38.5$ | 535469.938 | -0.040 | 456416.311 | -0.047 |
| 40(3,37) 39.5 | 39(3,36) 38.5 | 535473.551 | 0.002 | 456460.708 | 0.033 |
| 40(3,38) 40.5 | 39(3,37) 39.5 | 535543.825 | 0.214 | 456479.328 | -0.073 |
| 40(3,37) 40.5 | 39(3,36) 39.5 | 535547.193 | 0.059 | 456523.535 | 0.032 |
| 40( 2,39 ) 39.5 | 39(2,38) 38.5 | 535933.301 | -0.175 | 456408.744 | 0.016 |
| 40(2,39) 40.5 | $39(2,38) 39.5$ | 536008.198 | -0.162 | 456473.983 | -0.038 |
| 4010,40) 39.5 | 39(0,39) 38.5 | 536051.892 | -0.005 | 455552.165 | 0.037 |
| $40(0,40) 40.5$ | 39(0.39) 39.5 | \$36129.636 | 0.047 | 455623.133 | 0.039 |
| 40(2,38) 39.5 | 39(2,37) 38.5 | 536257.468 | -0.256 | 457714.563 | 0.006 |
| $40(2,38) 40.5$ | 39(2,37) 39.5 | 536329.514 | -0.101 | 457773.074 | 0.001 |
| 4(1) 39) 39.5 | 39(1,38) 38.5 | 538787.509 | -0.050 | 460065.916 | 0.013 |
| 40(1,39) 40.5 | $39(1,38) 39.5$ | 538855.606 | 0.126 | 460125.894 | 0.134 |
| 46(1,40) 45.5 | 45(1,45) 44.5 |  |  | 520356.902 | -0.073 |
| 46(1,40) 46.5 | 45(1,45) 45.5 |  |  | 520429.448 | -0.059 |
| 48(6,40) 45.5 | 454.39) 44.5 |  |  | 522054.939 | 0.036 |
| 46(6,41) 45.5 | $45(6,40) 44.5$ |  |  | 522054.939 | 0.036 |
| 4516,40) 46.5 | 45(6,39) 45.5 |  |  | 522117.919 | -0.010 |
| 46(6,41) 46.5 | 45(6,80) 45.5 |  |  | 522117.919 | -0.010 |
| 46(0,46) 45.5 | 4S(0,45) 44.5 |  |  | 523049.757 | -0.097 |
| 46(5,41) 45.5 | 45( 5,40 ) 44.5 |  |  | 523073.565 | 0.076 |
| 46(5,42) 45.5 | 45(5,41) 44.5 |  |  | 523073.565 | 0.089 |
| 46(0,46) 46.5 | 4510,45) 45.5 |  |  | 523122.613 | 0.034 |
| 46(5.41) 46.5 | 45(5,40) 45.5 |  |  | 523136.702 | 0.043 |
| 46( 5,42 ) 45.5 | 4S(5,41) 45.5 |  |  | 523136.702 | 0.056 |
| 46(2,45) 45.5 | $45(2,44) 44.5$ |  |  | 524413.130 | 0.289 |
| 46(2,45) 46.5 | $45(2.44) 45.5$ |  |  | 524478.717 | 0.184 |
| 46(2,44) 45.5 | 4S( 2,43 ) 44.5 |  |  | 526349.806 | -0.096 |
| 46(2,44) 46.5 | 45(2,43) 45.5 |  |  | 526407.079 | 0.009 |
| 46(4,43) 45.5 | $45(4,42) 44.5$ |  |  | 523895.018 | -0.045 |
| 46(4.42) 45.5 | 4S(4,41) 44.5 |  |  | 523896.534 | -0.014 |
| 46(4.43) 46.5 | 45(4,42) 45.5 |  |  | 523958.188 | -0.032 |
| 46(4,42) 46.5 | 45(4,41) 45.5 |  |  | 523959.707 | -0.020 |

${ }^{2}$ In MHz
shown, $\mathrm{SrNH} \mathrm{H}_{2}$ is planar molecule with $\mathrm{C}_{20}$ symmetry and a ${ }^{2} A_{1}$ ground siate. It also is a mearprolate asymmeric top. Consequently, the quanlum numbers used 10 label each transition are $N, K_{a}, K_{c}, S$, and $J$, in a case (b) coupling scheme. $N$ demotes the rotational angular momentum, while $J$ labels the spin-rotation interaction $(\hat{J}=\hat{N}+\hat{S})$. As is the case of any asymmetric top,
the degeneracy with respect to the $K$ quantum number is removed. $\mathbb{K}_{a}$ and $K_{c}$ correlate with $K$ in the limits of prolate and oblate symmetric tops, respectively, and although they are not good quantum numbers as such, they serve as labels for the energy levels. The dipole moment for $\mathrm{SrNH}_{2}$ lies along only the à axis; hence, a-lype dipole transitions are only allowed. The selection rules
$\Delta N= \pm 1, \Delta I= \pm 1, \Delta K_{a}=0$, and $\Delta K_{c}= \pm 1$ thus apply.

Estimates of the rotational constants for $\mathrm{SrNH}_{2}$ were made available so this research group by Brazier and Bernath prior to publication [12]. The search for pure-rotational hines of this molecule was greatly facilitated by these constants. Most transitions were predicted to be within $\pm 100 \mathrm{MHz}$ of the actual measurements. However, no spectroscopic constants existed for $\mathrm{Sr}^{2} \mathrm{ND}_{2}$, necessitating an extensive search through frequency space. This search was accomplished by first estimating the $A, B$, and $C$ rotational parameters for $\mathrm{SrND}_{2}$, scaling from those of $\mathrm{SrNH}_{2}$ by the mass difference. Transition frequencies were then predicted, and data were taken in 100 MHz increments over the entire range of $450-485 \mathrm{MHz}$. Spin-rotation doublets were consequently identified and harmonic relationsthips established among them. The harmonically related doublets, which correspond to particular $K_{0}$ components, were then fit with effective $B, D$, and $\gamma$ parameters. After a series of effective $B$ values were established, a relationship was looked for among the components by extrapolating back to the symmetric top limit. In this way, $K_{a}$ quantum numbers were assigned. Once the asymmetric top pattern was established, tramsition frequencies from additional $K_{\text {a }}$ components could be readily predicted and measured. Initial assignment of the $K_{a}=4$ components of $\mathrm{SrND}_{2}$ was also aided by its small asymmetry doubling at high $N$, as expected based on prior work done on $\mathrm{CaND}_{2}$ [16]. Asymmetry doubling of the higher $K_{s}$ components was not expected to be observed.

Spin statistics and line intensities were additionally helpful in the assignment of $K_{a}$ quantum numbers. The strongest lines were naturally attributed to the ground vibrational state. Moreover, for molecules with $C_{2 r}$ symmetry, fermion exchange (i.e., protons in the case of $\mathrm{SrNH}_{2}$ ) causes the odd $K_{a}$ components to be statistically favored over the even components by a $3: 1$ ratio. In the case of boson exchange (i.e., deuterons of $\mathrm{SrND}_{2}$ ), even $K_{0}$ components were favored over odd components by a $2: 1$ ratio. This alternating intensity ratio was quike evident in $\mathrm{SrNH}_{2}$, and aided in $K_{c}$ assignments. However, for $\mathrm{SrND}_{2}$, the 2:1 alteration in intensity was less obvious and was
not as defintive in identifying $K_{a}$ components. Furthermore, deuterium substitution results in a heavier molecule, and therefore lower energy leyeis. Consequently, components up to $K_{a}=8$ were easily observed in $\mathrm{SrND}_{3}$. For $\mathrm{SrNH}_{2}$, ooly $K_{a}$ components up to $\mathbb{K}_{n}=5$ were recorded.
It should be noted, as well, that magnetic and quadrupole hyperfine structure is possible for these molecules due to the interactions concerning the ${ }^{14} \mathrm{~N}(\mathrm{I}=1),{ }^{2} \mathrm{H}(\mathrm{I}=1 / 2)$ and $\mathrm{D}(\mathrm{I}=1)$ nuclei. In the frequency ranges investigated, the principal rotational levels examined for both molecules were quite high m $N$. Hyperfine spliting is not expected to be observed at these levels. In addition, signals arising from the other strontium isotopomers, namely the ${ }^{25} \mathrm{Sr}$ and ${ }^{37} \mathrm{Sr}$ analogs, are probably present. However, the spectra of these species were 100 weak to be realistically studied. (The strontium isolope ratio is ${ }^{88} \mathrm{Sr}:{ }^{87} \mathrm{Sr}:{ }^{85} \mathrm{Sr} \cong 83: 7: 10$.)

Sample specira of $\mathrm{SrNH}_{2}$ are presented in Figs. 1 and 2. Fig. 1 shows a section of the $N=36 \rightarrow 37$ rotational tramsition of the ground electronic and vibrational state near 496 GHz . The spectrum is a composite of 10 successive 100 MHz scans, totaling 1 GHz of frequency space. Evident in the scan are the $K_{a}=0,2$, and 3 components for this


Fig. 1. Spectrum of a section of the $N=36 \rightarrow 37$ rotationsa transition of $\mathrm{SrNH}_{2}\left(\mathrm{X}^{2} \mathrm{~A}_{1}\right)$ near 498 GHz Asymmerry dour bling is resolved in the $\mathbb{K}_{0}=2$ and 3 transitions, and the spinrotation spliting is apparent in every $K_{0}$ component. Asterisks zart umidenuifed lines, some which arise from vibrationally excited $\mathrm{SrNH}_{2}$. This spectrum is a composite of 10 scans. each covering 100 MHz in frequency with a duration of about 60 s .


Fig. 2. Spectrum of a section of the $N=40 \rightarrow 41$ transition of $\mathrm{SrND}_{2}\left(\mathrm{X}^{2} \mathrm{~A}_{1}\right)$ near 467 CHz . Spin-rotation interactions are observed in every $K_{0}$ componeni present ( $K_{0}=0,2.3$, and 4), some of which exhibit asymmetry doubling as well. Tweive 100 MH h seans were required to produce this spectrum, each $\sim 60$ s in duration.
transition. In each case, spin-rotation doublets are readily resolved and asymmetry doubling is apparent in the $K_{a}=2$ and 3 lines. It should be noted that the intensity of the $K_{a}=3$ components is clearly greater than that of the 0 or 2 components, as predicted for fermion exchange. Asterisks mark vibrational satellite transitions or unknown lines.

In Fig. 2 a typical spectrum of $\mathrm{SrND}_{2}$ is displayed. These data show a part of the $N=40 \rightarrow 41$ transition mear 467 GHH , which includes most of the $K_{a}=0,2,3$, and 4 componeats. (One set of $K_{a}=2$ doublets is not present as it occurs higher in frequency.) Here the $2: 1$ even $\mathbb{K}_{0}$ :odd $K$ boson ratio is apparent. Also, the asymmetry doubling in the $K_{\rho}=3$ components is on the same order of magnitude as the spin-rotation splititings, while it is totally collapsed for the $\mathbb{K}_{0}=4$ lines. This spectrum is a composite of 12 , 100 MHz scans.

## 4. Amalysis

The $\mathrm{SINH}_{2}$ and $\mathrm{SrND}_{2}$ spectra were analyzed using a slightly modified form of the S-reduced rotational Hamiltonian of Watson [20] in the $I$ r
basis, wilh the additional incorporation of a spimrotation tem, ie.e.

$$
\begin{equation*}
\hat{H}_{w I I}=\hat{H}_{x o t}+\hat{H}_{\text {es }} \tag{1}
\end{equation*}
$$

The first term concerns molecular frame rotation and a considerable mumber of centrifugal distortion corrections:

$$
\begin{align*}
& \hat{H}_{\mathrm{got}}=A N_{s}^{2}+B N_{y}^{2}+C N_{z}^{2}-D_{H} N^{4} \\
& -D_{N R} N^{2} N_{z}^{2}+d_{1} N^{2}\left(N_{+}^{2}+N_{-}^{2}\right)+d_{2} \\
& x\left(\mathbb{N}_{+}^{4}+\mathbb{N}_{-}\right)+H_{N} \mathbb{N}^{6}+H_{N K} \mathbb{N}^{4} N_{z}^{2} \\
& +H_{K N} N^{2} N_{z}^{4}+L_{N K} N^{-1} N_{z}^{4}+L_{N A R} N^{6} N_{s}^{2} \\
& +L_{\text {Kagu }} N^{2} N_{z}^{6}+P_{N K X} N^{+6} N_{z}^{6} \\
& +P_{N N K} N^{6} \mathbb{N}_{z}^{4}+P_{B N} N^{2} N_{z}^{8}+P_{N K} N^{6} N_{z}^{2} . \tag{2}
\end{align*}
$$

The second term involves only the diagonal terms in the spin-rotation temsor (as appropriate for $C_{20}$ symmetry), and one centrifugal distortion correction to the spin-rofation:

This Hamilionian was used to model the data, employing the least-squares fitting routine SPFIT, developed by Picketl and co-workers at JPL. To fil the data, only lower-order centrifugal distortion corrections to the rotation were initially employed. To achieve a better rms, higher-order terms were then added successively. A centrifugal distortion correction to the spin-rotation interaction was found necessary in the analysis of both $\mathrm{SrNH}_{2}$ and $\mathrm{SrND}_{2}$. Allogether, 14 centrifugal distortion terms were used to model $\mathrm{Sr}_{\mathrm{NH}}^{2}$; an almost identical set was needed 10 analyze $\mathrm{SrND}_{2}$. Only components up to $K_{a}=6$ were included in the $S i N D_{2}$ fit.

The final results of this data analysis are given in Table 2. The rms of the daia fiting was 92 kHz ( $\mathrm{SrNH}_{2}$ ) and $87 \mathrm{kHz}\left(\mathrm{SrND}_{2}\right)$, smaller than the ectimated expermental accuracy of 100 kHz Constants obtained from the optical study of Brazier and Bernath [12] are also shown in the table. (Ondy ihose centrifugal distortion parameters that can be meaningfully compared are listed.) The constants for $\mathrm{SrNH}_{2}$ from wo data sets are in good agreement. The only exception is $\varepsilon_{a}$, which is aboul a factor of two larger in the mm-wave fit than in the optical work. A subsequent reanalysis

Trole 2
Rotational constants for $\mathrm{SFNH}_{2}$ and $\mathrm{SrND}_{2}\left(\bar{X}^{2} A_{1}\right)^{\mathrm{a}}$

| Constant | $\mathrm{SrNH}_{2}$ | $\mathrm{SfND}_{2}$ | $\mathrm{SrNH}_{2}{ }^{\text {b }}$ optical |  |
| :---: | :---: | :---: | :---: | :---: |
| A | $394340(140)$ | $196565(12)$ | $394001(7)$ |  |
| \% | 8790.2961(27) | 5815.9704(49) | 6791.67169) |  |
| c | $6659.5159(29)$ | \$633.5686(30) | 6655.15(69) |  |
| $¢_{m}$ | 160.42.3) | 91.3(2.3) | $88(33)$ |  |
| $c_{0}$ | 59.740(86) | 51.526(79) | $54.1(2.5)$ |  |
| $t_{\text {ces }}$ | 89.657(81) | 76.841(69) | 86.42.5) |  |
| $A_{\text {ma }}^{5}$ | $-5.5(1.2) \times 10^{-4}$ | $-1.84(42) \times 10^{-6}$ |  |  |
| $D_{*}$ | $0.00607534(75)$ | $0.00410838(60)$ | 0.00580(23) |  |
| $D_{\text {ntr }}$ | $1.3595(14)$ | 0.91401(\%0) | 1.3583(69) |  |
| $d_{1}$ | -0.00015394(46) | -0.00017665(60) |  |  |
| $d_{2}$ | $-4.943(83) \times 10^{-5}$ | $-8.025(56) \times 10^{-5}$ |  |  |
| $h_{2}$ | $-1.31(38) \times 10^{-9}$ | B.52(20) $\times 10^{-9}$ |  |  |
| $\mathrm{n}_{3}$ | $-2.93(62) \times 10^{-10}$ | $4.62(53) \times 10^{-60}$ |  |  |
| $H_{\text {ana }}$ | $2.31(13) \times 10^{-5}$ | $1.641(42) \times 10^{-9}$ | $3.64(28) \times 10^{-5}$ | i, |
| $H_{\text {ra }}$ | -0.00620(18) | $-0.002087(63)$ | -0.00901(19) |  |
| $L_{\text {k }}$ | $1.6(1.3) \times 10^{-4}$ | $8.5(1.8) \times 10^{-8}$ |  |  |
| $L_{\text {Lra }}$ | $-1.383(45) \times 10^{-4}$ | $-5.5(2.2) \times 10^{-8}$ |  |  |
| $L_{\text {RAK }}$ | $-8.9(6.0) \times 10^{-30}$ | $-2.82(79) \times 10^{-10}$ |  |  |
| $P_{\text {Nax }}$ | $-1.00(22) \times 10^{-60}$ | $-5.1(25) \times 10^{-12}$ |  |  |
| $P_{\text {max }}$ | $2.26(29) \times 10^{-3}$ | $-7.3(2.5) \times 10^{-10}$ |  |  |
| $P_{\text {kn }}$ | - | $-1.24(31) \times 10^{-7}$ |  |  |
| $P_{\text {MRI }}$ | $3.3(1.5) \times 10^{-13}$ | - |  |  |
| Rows of fte | 0.092 | 0.087 |  |  |

${ }^{3}$ In MHze all errors are quoted to $3 \sigma$ and apply to the last quoted decinal place.
${ }^{6}$ Ref. [12].
by C.R. Brazier of their data (private commumication) indicates that the value of $\varepsilon_{\text {an }}$ is relatively insensitive to their overall fit. Fixing $\varepsilon_{e n}$ to the mmwave value near 160 MHz leads to virtually identical results in the optical analysis.

## 5. Discussion

This mm-wave study has resulted in refined spectroscopic constants for $\mathrm{SrNH}_{2}$ and the first such parameters for $\mathrm{Sr}_{\mathrm{ND}}^{2}$. These data indicate that both species are planar, as concluded by the previous optical investigations [10-12]. Evidence for planarity is found in the line intensities, which follow the pattern expected for $C_{2 x}$ symmetry and fermion or boson particle exchange. Other evidence for planar geometry is found in the inertial defects ( $A_{0}$ ), as shown in Table 3.

The imertial defect found for $\mathrm{SrNH}_{2}$ is $\Delta_{0}=0.180 \mathrm{amu} \dot{\AA}^{2}$. Although this value is not as small as that of some known planar species such as

Table 3
Inertial defects for $\mathrm{Sr}_{2} \mathrm{NH}_{2}$ and related species

| Molecule | $\Delta_{0}$ <br> $\left(\right.$ anau $\left.\dot{A}^{3}\right)$ | Ref. |
| :--- | :---: | :--- |
| $\mathrm{SrNH}_{2}$ | 0.180 | This work |
| $\mathrm{SNND}_{2}$ | 0.242 | This work |
| $\mathrm{CaNH}_{2}$ | 0.157 | $[16]$ |
| $\mathrm{CaND}_{2}$ | 0.210 | $[16]$ |
| $\mathrm{MgNH}_{2}$ | 0.078 | $[18]$ |
| $\mathrm{MgND}_{2}$ | 0.096 | $[181$ |
| $\mathrm{LiNH}_{2}$ | 0.115 | $[22]$ |
| $\mathrm{LND}_{2}$ | 0.150 | $[22]$ |
| $\mathrm{NaNH}_{2}$ | 0.079 | $[9]$ |
| $\mathrm{NH}_{2} \mathrm{CN}$ | -0.285 | $[23]$ |
| $\mathrm{ND}_{2} \mathrm{CN}$ | -0.746 | $[23]$ |
| $\mathrm{NH}_{2} \mathrm{NC}^{2}$ | -0.756 | $[24]$ |

$\mathrm{H}_{2} \mathrm{CO}(0.0577$; Ref. [21]), it is very close to those found for other planar amides. For example, the inerial defects for $\mathrm{CaNH}_{2}, \mathrm{NaNH}_{2}$ and $\mathrm{LiNH}_{2}$ are $0.157 \mathrm{amu} \AA^{2}$ [16], $0.079 \mathrm{amu} \AA^{2}$ [5], and 0.115 amu $\AA^{2}[22]$, respectively (see Table 3). The defect for $\mathrm{SrNH}_{2}$ is also positive. Other amide-type species such as $\mathrm{NH}_{2} \mathrm{CN}$ that show inversion have
large, negative values $[23,24]$. In fact, that of deuterated cyanamide is quite large and negative at $A_{0}=-0.746$ amu $\AA^{3}$. The inertial defect increases somewhat on deuteration for strontium amide ( $\mathrm{Sr}_{\mathrm{r}} \mathrm{ND}_{2}: A_{0}=0.242 \mathrm{amu} \AA^{2}$ ), but this trend is also observed for $\operatorname{CaND}_{2}\left(\Lambda_{0}=0.210\right.$ amu $\left.\AA^{2}\right)$, and $\operatorname{LND}_{2}\left(\Delta_{0}=0.150 \mathrm{amu} \AA^{2}\right)$, both planar species. Moreover, the value of $A_{0}$ does not change sign with deuteration, as found for non-planar formamide [25]. In this molecule, the inertial defect is small and positive ( 0.008 amu $\AA^{2}$ ), but changes sign on deuteration - an unusual property that indicates a non-planar structure.

Brazier and Bernath [12] estimated the geometry of $\mathrm{SrNH}_{2}$ by fixing the $\mathrm{N}-\mathrm{H}$ bond length to $1.041 \dot{\AA}$ - 3 hat of $\mathrm{NH}_{2}^{-}$. Because the spectrum of $\mathrm{Sr}_{\mathrm{ND}}^{2}$ has been measured, a true $r_{0}$ structure can be calculated for $\mathrm{SrNH}_{2}$ using the pure rotational data. The results of this calculation are presented in Table 4, along with the structure of $\mathrm{CaNH}_{2}$ from Brewster and Ziurys [16], obtained by an identical method. As the table shows, the N-H bond lengths and $\mathrm{H}-\mathrm{N}-\mathrm{H}$ angles for $\mathrm{SrNH}_{2}$ and $\mathrm{CaNH} \mathrm{H}_{2}$ are virually idenical. The only difference between these two species is the metal-nitrogen bond length, which increases for $\mathrm{SINH}_{2}$. This lengthening is expected, since the strontium atom is larger than that of calcium. These geometric similanities suggest that the $\mathrm{M}^{+} \mathrm{NH}_{2}^{-}$structure is
dominant for both species. Otherwise, more differences might be expected, for example, in the H -$\mathrm{N}-\mathrm{H}$ bond angle. The $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle of about $105^{\circ}$, found for both calcium and strontium amide, is a litule larger than the $100^{\circ}$ value estimated by Brazier and Bernath [12]; however, these authors fixed the H-N bond distance so be 0.02 $\dot{A}$ larger than found in the $r_{0}$ calculation.

Additional evidence for ionic bonding can be found in the spin-rotation constants for $\mathrm{SrNH}_{2}$. Although the unpaired electron in $\mathrm{SrNH}_{2}$ is to a first-order approximation located in an s-type orbital on the strontium atom, some degree of $\mathrm{p}, \mathrm{d}, \mathrm{f}$ ... character mixes into this orbital from nearby excited electronic states. The mixing occurs because of second-order spin-orbit coupling to the ground state from these excited states [26]. The result is that the spin-rotation constants are no longer merely mass-dependent terms. They refiect the magnitude of the spin-orbit coupling and consequently the anisotropic character of the orbital of the unpaired electron. Therefore, massnormalized spin-rotation constants can be a diagnostic of non-symmerric orbital character, and consequently, the deviation from ionic (spherical stype distribution) to covalent (non-spherical p,d ... distribution). This interpretation is especially useful for simple single valence electron systems, like $\mathrm{SrNH}_{2}$.

Table 4
Structures for $\mathrm{SrNH}_{2}$ and $\mathrm{CaNH}_{2}$

| Moiecule | $\begin{aligned} & { }^{\mathrm{NN}}(\mathrm{~A}) \\ & (\mathrm{A}) \end{aligned}$ | $\mathrm{rman}_{\mathrm{m}}$ <br> (A) | $\begin{aligned} & 011 \mathrm{~N} 1 \\ & \text { (degress) } \end{aligned}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{SrNH} \mathrm{H}_{2}$ | 1.021 | 2.256 | 105.4 | This work |
|  | $1.041^{8}$ | 2.247 | 100.0 | [12] |
| $\mathrm{CaNH}_{2}$ | 1.018 | 2.126 | 105.8 | [16] |

"Fired bond lemgth

Table 5
Normalizad spip-rotavion conssanis for strontium radicals

| Molecule | Ground state | \%/B | 1/2( $\left.5_{50}+c_{40}\right) / B$ | 1/2( $\left.5_{\text {E }} / B+\varphi_{\text {col }} / C\right)$ | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Str | ${ }^{2} \Sigma$ | 0.010 | - | - | [27] |
| SrOH | ${ }^{25}$ | 0.010 | - | - | [28] |
| $\mathrm{SrNH}_{2}$ | ${ }^{2} A_{1}$ | - | - | 0.011 | This work |
| SrCCH | ${ }^{2} \mathrm{E}$ | 0.020 | - | - | [30] |
| $\mathrm{SrCH}_{3}$ | ${ }^{2}{ }_{\text {A }}^{1}$ | - | 0.021 | - | [8] |
| SrH | ${ }^{2} \mathrm{E}$ | 0.034 | - | - | [29] |

A list of normalized spin-rotation constants for simple strontum-containing radicals is presented in Table 5. The molecules involved have either ${ }^{2} \Sigma$ or ${ }^{2} A$ ground electronic states, and hence there is a direet comparison. Also, in should be noted that $\varepsilon_{b s}$ and $\varepsilon_{c c}$ are the important spin-sotation components for symmetric and asymmetric tops, since the second-order spin-orbil coupling occurs through the $\hat{L}_{x}$ operator. The species in Table 5 range from very ionic species (SrF, SrOH) to a primarily covalent one ( SrH ). The normalized spin-rotation parameters have values of 0.010 for $\mathrm{SrF}[27]$ and $\mathrm{SrOH}[28]$ while that of SrH is larger: 0.034 [29]. Those of $\mathrm{SrCH}_{3}$ [8] and SrCCH [30] fall in between, about 0.02 . Curiously, the normalized constant for SrNH is 0.011 - very close to that of SrF and SrOH . A similar trend has been found for $\mathrm{CaNH}_{2}$ in comparison with other calcium radicals [16]. Consequently, the nature of the orbital of the unpaired electron in $\mathrm{SrNH}_{2}$ is very close to that of the hydroxide and the fluoride, and the $\mathrm{Sr}^{+} \mathrm{NH}_{2}^{-}$ configuration is probably a very good approximation of the structure of this radical.

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Table S1. Complete List of $\mathrm{SrNH}_{2}$ Rotational Transition Frequencies ${ }^{\text {a }}$

| N | $\mathrm{K}_{\mathbf{8}}{ }^{\text {a }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {b }}$ | J' | $\leftarrow$ | $\mathrm{N}^{\mathrm{p}}$ | $\mathrm{K}_{\mathrm{s}}{ }^{\text {m }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $\mathrm{J}^{\prime \prime}$ | $V_{\text {obs }}$ | $V_{\text {obs }}$ calc |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 17 | 1 | 17 | 16.5 |  | 16 | 1 | 16 | 15.5 | 227325.149 | -0.031 |
| 17 | 1 | 17 | 17.5 |  | 16 | 1 | 16 | 16.5 | 227407.200 | 0.011 |
| 17 | 3 | 15 | 16.5 |  | 16 | 3 | 14 | 15.5 | 228063.014 | 0.001 |
| 17 | 3 | 14 | 16.5 |  | 16 | 3 | 13 | 15.5 | 228063.054 | -0.008 |
| 17 | 3 | 15 | 17.5 |  | 16 | 3 | 14 | 16.5 | 228135.072 | 0.142 |
| 17 | 3 | 14 | 17.5 |  | 16 | 3 | 13 | 16.5 | 228135.062 | 0.084 |
| 17 | 1 | 16 | 16.5 |  | 16 | 1 | 15 | 15.5 | 229549.898 | 0.072 |
| 17 | 1 | 16 | 17.5 |  | 16 | 1 | 15 | 16.5 | 229616.847 | -0.031 |
| 18 | 1 | 18 | 17.5 |  | 17 | 1 | 17 | 16.5 | 240683.871 | -0.041 |
| 18 | 1 | 18 | 18.5 |  | 17 | 1 | 17 | 17.5 | 240765.975 | 0.006 |
| 18 | 1 | 17 | 17.5 |  | 17 | 1 | 16 | 16.5 | 243038.275 | 0.082 |
| 18 | 1 | 17 | 18.5 |  | 17 | 1 | 16 | 17.5 | 243105.303 | 0.010 |
| 26 | 1 | 26 | 25.5 |  | 25 | 1 | 25 | 24.5 | 347444.373 | 0.075 |
| 26 | 1 | 26 | 26.5 |  | 25 | 1 | 25 | 25.5 | 347526.640 | -0.009 |
| 26 | 3 | 24 | 25.5 |  | 25 | 3 | 23 | 24.5 | 348591.439 | -0.037 |
| 26 | 3 | 23 | 25.5 |  | 25 | 3 | 22 | 24.5 | 348591.755 | -0.135 |
| 26 | 3 | 24 | 26.5 |  | 25 | 3 | 23 | 25.5 | 348664.608 | -0.172 |
| 26 | 3 | 23 | 26.5 |  | 25 | 3 | 22 | 25.5 | 348665.013 | -0.170 |
| 26 | 2 | 24 | 26.5 |  | 25 | 2 | 23 | 25.5 | 349099.594 | 0.006 |
| 26 | 0 | 26 | 25.5 |  | 25 | 0 | 25 | 24.5 | 349133.784 | -0.056 |
| 26 | 0 | 26 | 26.5 |  | 25 | 0 | 25 | 25.5 | 349209.657 | -0.157 |
| 26 | 1 | 25 | 25.5 |  | 25 | 1 | 24 | 24.5 | 350830.108 | 0.066 |
| 26 | 1 | 25 | 26.5 |  | 25 | 1 | 24 | 25.5 | 350897.382 | -0.063 |
| 27 | 5 | 22 | 26.5 |  | 26 | 5 | 21 | 25.5 | 360548.455 | -0.294 |
| 27 | 5 | 23 | 26.5 |  | 26 | 5 | 22 | 25.5 | 360548.455 | -0.294 |
| 27 | 5 | 22 | 27.5 |  | 26 | 5 | 21 | 26.5 | 360619.926 | -0.231 |
| 27 | 5 | 23 | 27.5 |  | 26 | 5 | 22 | 26.5 | 360619.926 | -0.231 |
| 27 | 1 | 27 | 26.5 |  | 26 | 1 | 26 | 25.5 | 360773.464 | 0.042 |
| 27 | 1 | 27 | 27.5 |  | 26 | 1 | 26 | 26.5 | 360855.787 | -0.019 |
| 27 | 4 | 24 | 26.5 |  | 26 | 4 | 23 | 25.5 | 361383.592 | 0.195 |
| 27 | 4 | 23 | 26.5 |  | 26 | 4 | 22 | 25.5 | 361383.592 | 0.193 |
| 27 | 4 | 24 | 27.5 |  | 26 | 4 | 23 | 26.5 | 361456.191 | 0.257 |
| 27 | 4 | 23 | 27.5 |  | 26 | 4 | 22 | 26.5 | 361456.191 | 0.256 |
| 27 | 3 | 25 | 26.5 |  | 26 | 3 | 24 | 25.5 | 361967.630 | 0.037 |
| 27 | 3 | 24 | 26.5 |  | 26 | 3 | 23 | 25.5 | 361967.992 | -0.101 |
| 27 | 3 | 25 | 27.5 |  | 26 | 3 | 24 | 26.5 | 362040.798 | -0.162 |
| 27 | 3 | 24 | 27.5 |  | 26 | 3 | 23 | 26.5 | 362041.228 | -0.220 |
| 27 | 2 | 26 | 26.5 |  | 26 | 2 | 25 | 25.5 | 362323.244 | 0.047 |
| 27 | 2 | 26 | 27.5 |  | 26 | 2 | 25 | 26.5 | 362397.581 | -0.026 |
| 27 | 2 | 25 | 26.5 |  | 26 | 2 | 24 | 25.5 | 362424.028 | 0.052 |
| 27 | 2 | 25 | 27.5 |  | 26 | 2 | 24 | 26.5 | 362497.030 | 0.019 |
| 27 | 0 | 27 | 26.5 |  | 26 | 0 | 26 | 25.5 | 362520.860 | -0.063 |
| 27 | 0 | 27 | 27.5 |  | 26 | 0 | 26 | 26.5 | 362596.848 | -0.149 |
| 27 | 1 | 26 | 26.5 |  | 26 | 1 | 25 | 25.5 | 364287.356 | 0.082 |
| 27 | 1 | 26 | 27.5 |  | 26 | 1 | 25 | 26.5 | 364354.663 | -0.048 |
| 28 | 5 | 23 | 27.5 |  | 27 | 5 | 22 | 26.5 | 373871.796 | -0.088 |
| 28 | 5 | 24 | 27.5 |  | 27 | 5 | 23 | 26.5 | 373871.796 | -0.088 |
| 28 | 5 | 23 | 28.5 |  | 27 | 5 | 22 | 27.5 | 373943.386 | -0.084 |

Table S1. Cont'd.

| $\mathrm{N}^{2}$ | $K_{\text {a }}{ }^{\circ}$ | $\mathbb{K}_{\mathrm{c}}{ }^{\text {e }}$ | J | $\leftarrow$ | N" | $\mathrm{K}_{\mathrm{g}}{ }^{19}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {e }}$ | $\mathrm{J}^{\prime \prime}$ | $V_{\text {obs }}$ | $\nu_{\text {obs - calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 28 | 5 | 24 | 28.5 |  | 27 | 5 | 23 | 27.5 | 373943.386 | -0.084 |
| 28 | 1 | 28 | 27.5 |  | 27 | 1 | 27 | 26.5 | 374098.585 | 0.074 |
| 28 | 1 | 28 | 28.5 |  | 27 | 1 | 27 | 27.5 | 374180.918 | -0.009 |
| 28 | 4 | 25 | 27.5 |  | 27 | 4 | 24 | 26.5 | 374735.178 | 0.143 |
| 28 | 4 | 24 | 27.5 |  | 27 | 4 | 23 | 26.5 | 374735.178 | 0.141 |
| 28 | 4 | 25 | 28.5 |  | 27 | 4 | 24 | 27.5 | 374807.838 | 0.155 |
| 28 | 4 | 24 | 28.5 |  | 27 | 4 | 23 | 27.5 | 374807.838 | 0.154 |
| 28 | 3 | 26 | 27.5 |  | 27 | 3 | 25 | 26.5 | 375339.976 | -0.034 |
| 28 | 3 | 25 | 27.5 |  | 27 | 3 | 24 | 26.5 | 375340.381 | -0.229 |
| 28 | 3 | 26 | 28.5 |  | 27 | 3 | 25 | 27.5 | 375413.417 | -0.015 |
| 28 | 3 | 25 | 28.5 |  | 27 | 3 | 24 | 27.5 | 375413.834 | -0.184 |
| 28 | 2 | 27 | 27.5 |  | 27 | 2 | 26 | 26.5 | 375706.080 | 0.138 |
| 28 | 2 | 27 | 28.5 |  | 27 | 2 | 26 | 27.5 | 375780.402 | 0.003 |
| 28 | 2 | 26 | 27.5 |  | 27 | 2 | 25 | 26.5 | 375818.323 | 0.056 |
| 28 | 2 | 26 | 28.5 |  | 27 | 2 | 25 | 27.5 | 375891.258 | 0.013 |
| 28 | 0 | 28 | 27.5 |  | 27 | 0 | 27 | 26.5 | 375903.139 | -0.059 |
| 28 | 0 | 28 | 28.5 |  | 27 | 0 | 27 | 27.5 | 375979.245 | -0.130 |
| 28 | 1 | 27 | 27.5 |  | 27 | 1 | 26 | 26.5 | 377740.326 | 0.067 |
| 28 | 1 | 27 | 28.5 |  | 27 | 1 | 26 | 27.5 | 377807.690 | -0.040 |
| 29 | 5 | 24 | 28.5 |  | 28 | 5 | 23 | 27.5 | 387191.863 | 0.363 |
| 29 | 5 | 25 | 28.5 |  | 28 | 5 | 24 | 27.5 | 387191.863 | 0.363 |
| 29 | 5 | 24 | 29.5 |  | 28 | 5 | 23 | 28.5 | 387263.546 | 0.302 |
| 29 | 5 | 25 | 29.5 |  | 28 | 5 | 24 | 28.5 | 387263.546 | 0.302 |
| 29 | 1 | 29 | 28.5 |  | 28 | 1 | 28 | 27.5 | 387419.519 | 0.102 |
| 29 | 1 | 29 | 29.5 |  | 28 | 1 | 28 | 28.5 | 387501.885 | 0.020 |
| 29 | 4 | 26 | 28.5 |  | 28 | 4 | 25 | 27.5 | 388082.992 | 0.071 |
| 29 | 4 | 25 | 28.5 |  | 28 | 4 | 24 | 27.5 | 388082.992 | 0.069 |
| 29 | 4 | 26 | 29.5 |  | 28 | 4 | 25 | 28.5 | 388155.746 | 0.081 |
| 29 | 4 | 25 | 29.5 |  | 28 | 4 | 24 | 28.5 | 388155.746 | 0.079 |
| 29 | 3 | 27 | 28.5 |  | 28 | 3 | 26 | 27.5 | 388708.664 | 0.075 |
| 29 | 3 | 26 | 28.5 |  | 28 | 3 | 25 | 27.5 | 388709.234 | -0.070 |
| 29 | 3 | 27 | 29.5 |  | 28 | 3 | 26 | 28.5 | 388782.077 | 0.020 |
| 29 | 3 | 26 | 29.5 |  | 28 | 3 | 25 | 28.5 | 388782.640 | -0.116 |
| 29 | 2 | 28 | 28.5 |  | 28 | 2 | 27 | 27.5 | 389084.607 | 0.063 |
| 29 | 2 | 28 | 29.5 |  | 28 | 2 | 27 | 28.5 | 389159.042 | -0.003 |
| 29 | 2 | 27 | 28.5 |  | 28 | 2 | 26 | 27.5 | 389209.312 | 0.057 |
| 29 | 0 | 29 | 28.5 |  | 28 | 0 | 28 | 27.5 | 389280.444 | -0.046 |
| 29 | 2 | 27 | 29.5 |  | 28 | 2 | 26 | 28.5 | 389282.188 | 0.018 |
| 29 | 0 | 29 | 29.5 |  | 28 | 0 | 28 | 28.5 | 389356.659 | -0.114 |
| 29 | 1 | 28 | 28.5 |  | 28 | 1 | 27 | 27.5 | 391188.901 | 0.061 |
| 29 | 1 | 28 | 29.5 |  | 28 | 1 | 27 | 28.5 | 391256.327 | -0.018 |
| 33 | 1 | 33 | 32.5 |  | 32 | 1 | 32 | 31.5 | 440658.322 | 0.088 |
| 33 | 1 | 33 | 33.5 |  | 32 | 1 | 32 | 32.5 | 440740.880 | 0.067 |
| 33 | 4 | 30 | 32.5 |  | 32 | 4 | 29 | 31.5 | 441434.099 | -0.084 |
| 33 | 4 | 29 | 32.5 |  | 32 | 4 | 28 | 31.5 | 441434.099 | -0.089 |
| 33 | 4 | 30 | 33.5 |  | 32 | 4 | 29 | 32.5 | 441507.074 | -0.128 |
| 33 | 4 | 29 | 33.5 |  | 32 | 4 | 28 | 32.5 | 441507.074 | -0.132 |
| 33 | 3 | 31 | 32.5 |  | 32 | 3 | 30 | 31.5 | 442141.702 | -0.037 |

Table S1. Cont'd.

| $\mathrm{N}^{\prime}$ | $K_{\text {a }}{ }^{\text {a }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | J' | $\leftarrow$ | $\mathrm{N}^{\prime \prime}$ | $\mathrm{K}_{\mathrm{a}}{ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {f }}$ | $J^{81}$ | $V_{\text {obs }}$ | Vobs-calc |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 33 | 3 | 30 | 32.5 |  | 32 | 3 | 29 | 31.5 | 442143.149 | 0.045 |
| 33 | 3 | 31 | 33.5 |  | 32 | 3 | 30 | 32.5 | 442215.265 | -0.061 |
| 33 | 3 | 30 | 33.5 |  | 32 | 3 | 29 | 32.5 | 442216.696 | 0.032 |
| 33 | 2 | 32 | 32.5 |  | 32 | 2 | 31 | 31.5 | 442554.612 | 0.053 |
| 33 | 2 | 32 | 33.5 |  | 32 | 2 | 31 | 32.5 | 442629.225 | 0.011 |
| 33 | 0 | 33 | 32.5 |  | 32 | 0 | 32 | 31.5 | 442736.271 | -0.046 |
| 33 | 2 | 31 | 32.5 |  | 32 | 2 | 30 | 31.5 | 442737.826 | 0.042 |
| 33 | 2 | 31 | 33.5 |  | 32 | 2 | 30 | 32.5 | 442810.399 | 0.009 |
| 33 | 0 | 33 | 33.5 |  | 32 | 0 | 32 | 32.5 | 442812.892 | -0.172 |
| 33 | 1 | 32 | 32.5 |  | 32 | 1 | 31 | 31.5 | 444936.027 | 0.055 |
| 33 | 1 | 32 | 33.5 |  | 32 | 1 | 31 | 32.5 | 445003.655 | 0.036 |
| 34 | 1 | 34 | 33.5 |  | 33 | 1 | 33 | 32.5 | 453956.064 | 0.067 |
| 34 | 1 | 34 | 34.5 |  | 33 | 1 | 33 | 33.5 | 454038.714 | 0.104 |
| 34 | 4 | 31 | 33.5 |  | 33 | 4 | 30 | 32.5 | 454761.198 | -0.040 |
| 34 | 4 | 30 | 33.5 |  | 33 | 4 | 29 | 32.5 | 454761.198 | -0.046 |
| 34 | 3 | 32 | 33.5 |  | 33 | 3 | 31 | 32.5 | 455489.057 | 0.015 |
| 34 | 3 | 31 | 33.5 |  | 33 | 3 | 30 | 32.5 | 455490.679 | 0.053 |
| 34 | 3 | 32 | 34.5 |  | 33 | 3 | 31 | 33.5 | 455562.643 | -0.003 |
| 34 | 3 | 31 | 34.5 |  | 33 | 3 | 30 | 33.5 | 455564.239 | 0.039 |
| 34 | 2 | 33 | 33.5 |  | 33 | 2 | 32 | 32.5 | 455910.276 | 0.051 |
| 34 | 2 | 33 | 34.5 |  | 33 | 2 | 32 | 33.5 | 455984.940 | 0.024 |
| 34 | 0 | 34 | 33.5 |  | 33 | 0 | 33 | 32.5 | 456086.011 | -0.056 |
| 34 | 2 | 32 | 33.5 |  | 33 | 2 | 31 | 32.5 | 456110.482 | 0.025 |
| 34 | 0 | 34 | 34.5 |  | 33 | 0 | 33 | 33.5 | 456162.890 | -0.049 |
| 34 | 2 | 32 | 34.5 |  | 33 | 2 | 31 | 33.5 | 456183.016 | 0.042 |
| 34 | 1 | 33 | 33.5 |  | 33 | 1 | 32 | 32.5 | 458360.213 | 0.042 |
| 34 | 1 | 33 | 34.5 |  | 33 | 1 | 32 | 33.5 | 458427.912 | 0.057 |
| 35 | 1 | 35 | 34.5 |  | 34 | 1 | 34 | 33.5 | 467248.750 | 0.062 |
| 35 | 1 | 35 | 35.5 |  | 34 | 1 | 34 | 34.5 | 467331.414 | 0.080 |
| 35 | 4 | 32 | 34.5 |  | 34 | 4 | 31 | 33.5 | 468083.633 | -0.081 |
| 35 | 4 | 31 | 34.5 |  | 34 | 4 | 30 | 33.5 | 468083.633 | -0.088 |
| 35 | 4 | 32 | 35.5 |  | 34 | 4 | 31 | 34.5 | 468156.730 | -0.090 |
| 35 | 4 | 31 | 35.5 |  | 34 | 4 | 30 | 34.5 | 468156.730 | -0.097 |
| 35 | 3 | 33 | 34.5 |  | 34 | 3 | 32 | 33.5 | 468831.739 | 0.064 |
| 35 | 3 | 32 | 34.5 |  | 34 | 3 | 31 | 33.5 | 468833.549 | 0.043 |
| 35 | 3 | 33 | 35.5 |  | 34 | 3 | 32 | 34.5 | 468905.332 | 0.041 |
| 35 | 3 | 32 | 35.5 |  | 34 | 3 | 31 | 34.5 | 468907.106 | 0.017 |
| 35 | 2 | 34 | 34.5 |  | 34 | 2 | 33 | 33.5 | 469260.888 | 0.025 |
| 35 | 2 | 34 | 35.5 |  | 34 | 2 | 33 | 34.5 | 469335.598 | 0.011 |
| 35 | 0 | 35 | 34.5 |  | 34 | 0 | 34 | 33.5 | 469429.731 | -0.056 |
| 35 | 0 | 35 | 35.5 |  | 34 | 0 | 34 | 34.5 | 469506.753 | -0.034 |
| 35 | 2 | 33 | 34.5 |  | 34 | 2 | 32 | 33.5 | 469479.107 | 0.002 |
| 35 | 2 | 33 | 35.5 |  | 34 | 2 | 32 | 34.5 | 469551.571 | 0.043 |
| 35 | 1 | 34 | 34.5 |  | 34 | 1 | 33 | 33.5 | 471779.049 | 0.027 |
| 35 | 1 | 34. | 35.5 |  | 34 | 1 | 33 | 34.5 | 471846.813 | 0.070 |
| 36 | 1 | 36 | 35.5 |  | 35 | 1 | 35 | 34.5 | 480536.220 | 0.060 |
| 36 | 1 | 36 | 36.5 |  | 35 | 1 | 35 | 35.5 | 480618.918 | 0.078 |
| 36 | 4 | 33 | 35.5 |  | 35 | 4 | 32 | 34.5 | 481401.411 | -0.064 |

Table SI. Cont'd.

| N | $\mathrm{K}_{\mathrm{e}}{ }^{\prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text { }}$ | J | $\leftarrow$ | $\mathrm{N}^{\prime \prime}$ | $\mathrm{K}_{\mathrm{a}}{ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $\mathrm{J}^{\prime \prime}$ | $V_{\text {obs }}$ | $\mathrm{V}_{\text {obs }}$ calc |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 36 | 4 | 32 | 35.5 |  | 35 |  | 31 | 34.5 | 481401.411 | -0.072 |
| 36 | 4 | 33 | 36.5 |  | 35 | 4 | 32 | 35.5 | 481474.485 | -0.129 |
| 36 | 4 | 32 | 36.5 |  | 35 | 4 | 31 | 35.5 | 481474.485 | -0.138 |
| 36 | 3 | 34 | 35.5 |  | 35 | 3 | 33 | 34.5 | 482169.560 | 0.061 |
| 36 | 3 | 33 | 35.5 |  | 35 | 3 | 32 | 34.5 | 482171.681 | 0.073 |
| 36 | 3 | 34 | 36.5 |  | 35 | 3 | 33 | 35.5 | 482243.157 | 0.032 |
| 36 | 3 | 33 | 36.5 |  | 35 | 3 | 32 | 35.5 | 482245.226 | 0.030 |
| 36 | 2 | 35 | 35.5 |  | 35 | 2 | 34 | 34.5 | 482606.320 | -0.004 |
| 36 | 2 | 35 | 36.5 |  | 35 | 2 | 34 | 35.5 | 482681.067 | -0.014 |
| 36 | 0 | 36 | 35.5 |  | 35 | 0 | 35 | 34.5 | 482767.244 | -0.059 |
| 36 | 2 | 34 | 35.5 |  | 35 | 2 | 33 | 34.5 | 482843.561 | -0.046 |
| 36 | 0 | 36 | 36.5 |  | 35 | 0 | 35 | 35.5 | 482844.432 | -0.003 |
| 36 | 2 | 34 | 36.5 |  | 35 | 2 | 33 | 35.5 | 482915.975 | 0.044 |
| 36 | 1 | 35 | 35.5 |  | 35 | 1 | 34 | 34.5 | 485192.391 | 0.023 |
| 36 | 1 | 35 | 36.5 |  | 35 | 1 | 34 | 35.5 | 485260.207 | 0.080 |
| 37 | 1 | 37 | 36.5 |  | 36 | 1 | 36 | 35.5 | 493818.293 | 0.029 |
| 37 | 1 | 37 | 37.5 |  | 36 | 1 | 36 | 36.5 | 493901.044 | 0.065 |
| 37 | 4 | 34 | 36.5 |  | 36 | 4 | 33 | 35.5 | 494714.320 | -0.064 |
| 37 | 4 | 33 | 36.5 |  | 36 | 4 | 32 | 35.5 | 494714.320 | -0.074 |
| 37 | 4 | 34 | 37.5 |  | 36 | 4 | 33 | 36.5 | 494787.442 | -0.109 |
| 37 | 4 | 33 | 37.5 |  | 36 | 4 | 32 | 36.5 | 494787.442 | -0.120 |
| 37 | 3 | 35 | 36.5 |  | 36 | 3 | 34 | 35.5 | 495502.415 | 0.037 |
| 37 | 3 | 34 | 36.5 |  | 36 | 3 | 33 | 35.5 | 495504.861 | 0.065 |
| 37 | 3 | 35 | 37.5 |  | 36 | 3 | 34 | 36.5 | 495576.055 | 0.045 |
| 37 | 3 | 34 | 37.5 |  | 36 | 3 | 33 | 36.5 | 495578.469 | 0.083 |
| 37 | 2 | 36 | 36.5 |  | 36 | 2 | 35 | 35.5 | 495946.427 | -0.035 |
| 37 | 2 | 36 | 37.5 |  | 36 | 2 | 35 | 36.5 | 496021.227 | -0.025 |
| 37 | 0 | 37 | 36.5 |  | 36 | 0 | 36 | 35.5 | 496098.367 | -0.078 |
| 37 | 0 | 37 | 37.5 |  | 36 | 0 | 36 | 36.5 | 496175.713 | 0.002 |
| 37 | 2 | 35 | 36.5 |  | 36 | 2 | 34 | 35.5 | 496203.779 | -0.062 |
| 37 | 2 | 35 | 37.5 |  | 36 | 2 | 34 | 36.5 | 496276.066 | 0.003 |
| 37 | 1 | 36 | 36.5 |  | 36 | 1 | 35 | 35.5 | 498600.058 | 0.007 |
| 37 | 1 | 36 | 37.5 |  | 36 | 1 | 35 | 36.5 | 498667.955 | 0.105 |
| 38 | 1 | 38 | 37.5 |  | 37 | 1 | 37 | 36.5 | 507094.875 | 0.021 |
| 38 | 1 | 38 | 38.5 |  | 37 | 1 | 37 | 37.5 | 507177.667 | 0.063 |
| 38 | 4 | 35 | 37.5 |  | 37 | 4 | 34 | 36.5 | 508022.314 | 0.008 |
| 38 | 4 | 34 | 37.5 |  | 37 | 4 | 33 | 36.5 | 508022.314 | -0.005 |
| 38 | 4 | 35 | 38.5 |  | 37 | 4 | 34 | 37.5 | 508095.426 | -0.070 |
| 38 | 4 | 34 | 38.5 |  | 37 | 4 | 33 | 37.5 | 508095.426 | -0.083 |
| 38 | 3 | 36 | 37.5 |  | 37 | 3 | 35 | 36.5 | 508830.216 | 0.040 |
| 38 | 3 | 35 | 37.5 |  | 37 | 3 | 34 | 36.5 | 508833.022 | 0.084 |
| 38 | 3 | 36 | 38.5 |  | 37 | 3 | 35 | 37.5 | 508903.895 | 0.085 |
| 38 | 3 | 35 | 38.5 |  | 37 | 3 | 34 | 37.5 | 508906.610 | 0.084 |
| 38 | 2 | 37 | 37.5 |  | 37 | 2 | 36 | 36.5 | 509281.052 | -0.079 |
| 38 | 2 | 37 | 38.5 |  | 37 | 2 | 36 | 37.5 | 509355.887 | -0.065 |
| 38 | 0 | 38 | 37.5 |  | 37 | 0 | 37 | 36.5 | 509422.968 | -0.070 |
| 38 | 0 | 38 | 38.5 |  | 37 | 0 | 37 | 37.5 | 509500.457 | 0.014 |
| 38 | 2 | 36 | 37.5 |  | 37 | 2 | 35 | 36.5 | 509559.561 | -0.126 |

Table S1. Cont'd.

| N | $\mathbf{K}_{\mathrm{a}}{ }^{\text {a }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | J | $t$ | $\mathrm{N}^{\text {a }}$ | $\mathrm{K}_{8}{ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {8 }}$ | $\mathrm{J}^{\prime \prime}$ | $V_{\text {obs }}$ | $V_{\text {obs-calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 38 | 2 | 36 | 38.5 |  | 37 | 2 | 35 | 37.5 | 509631.797 | -0.005 |
| 38 | 1 | 37 | 37.5 |  | 37 | 1 | 36 | 36.5 | 512001.926 | 0.010 |
| 38 | 1 | 37 | 38.5 |  | 37 | 1 | 36 | 37.5 | 512069.872 | 0.118 |
| 39 | 1 | 39 | 38.5 |  | 38 | 1 | 38 | 37.5 | 520365.758 | -0.026 |
| 39 | 1 | 39 | 39.5 |  | 38 | 1 | 38 | 38.5 | 520448.607 | 0.038 |
| 39 | 4 | 36 | 38.5 |  | 38 | 4 | 35 | 37.5 | 521325.144 | 0.038 |
| 39 | 4 | 35 | 38.5 |  | 38 | 4 | 34 | 37.5 | 521325.144 | 0.023 |
| 39 | 4 | 36 | 39.5 |  | 38 | 4 | 35 | 38.5 | 521398.298 | -0.017 |
| 39 | 4 | 35 | 39.5 |  | 38 | 4 | 34 | 38.5 | 521398.298 | -0.032 |
| 39 | 3 | 37 | 38.5 |  | 38 | 3 | 36 | 37.5 | 522152.754 | $<0.000$ |
| 39 | 3 | 36 | 38.5 |  | 38 | 3 | 35 | 37.5 | 522155.936 | 0.036 |
| 39 | 3 | 37 | 39.5 |  | 38 | 3 | 36 | 38.5 | 522226.412 | 0.023 |
| 39 | 3 | 36 | 39.5 |  | 38 | 3 | 35 | 38.5 | 522229.578 | 0.095 |
| 39 | 2 | 38 | 38.5 |  | 38 | 2 | 37 | 37.5 | 522610.032 | -0.152 |
| 39 | 2 | 38 | 39.5 |  | 38 | 2 | 37 | 38.5 | 522684.946 | -0.091 |
| 39 | 0 | 39 | 38.5 |  | 38 | 0 | 38 | 37.5 | 522740.837 | -0.075 |
| 39 | 0 | 39 | 39.5 |  | 38 | 0 | 38 | 38.5 | 522818.524 | 0.065 |
| 39 | 2 | 37 | 38.5 |  | 38 | 2 | 36 | 37.5 | 522910.859 | -0.163 |
| 39 | 2 | 37 | 39.5 |  | 38 | 2 | 36 | 38.5 | 522982.953 | -0.074 |
| 39 | 1 | 38 | 38.5 |  | 38 | 1 | 37 | 37.5 | 525397.784 | -0.020 |
| 39 | 1 | 38 | 39.5 |  | 38 | 1 | 37 | 38.5 | 525465.782 | 0.100 |
| 40 | 1 | 40 | 39.5 |  | 39 | 1 | 39 | 38.5 | 533630.868 | -0.037 |
| 40 | 1 | 40 | 40.5 |  | 39 | 1 | 39 | 39.5 | 533713.743 | 0.017 |
| 40 | 4 | 37 | 39.5 |  | 39 | 4 | 36 | 38.5 | 534622.704 | 0.053 |
| 40 | 4 | 36 | 39.5 |  | 39 | 4 | 35 | 38.5 | 534622.704 | 0.035 |
| 40 | 4 | 37 | 40.5 |  | 39 | 4 | 36 | 39.5 | 534695.931 | 0.058 |
| 40 | 4 | 36 | 40.5 |  | 39 | 4 | 35 | 39.5 | 534695.931 | 0.039 |
| 40 | 3 | 38 | 39.5 |  | 39 | 3 | 37 | 38.5 | 535469.938 | -0.040 |
| 40 | 3 | 37 | 39.5 |  | 39 | 3 | 36 | 38.5 | 535473.551 | -0.002 |
| 40 | 3 | 38 | 40.5 |  | 39 | 3 | 37 | 39.5 | 535543.825 | 0.214 |
| 40 | 3 | 37 | 40.5 |  | 39 | 3 | 36 | 39.5 | 535547.193 | 0.069 |
| 40 | 2 | 39 | 39.5 |  | 39 | 2 | 38 | 38.5 | 535933.301 | -0.175 |
| 40 | 2 | 39 | 40.5 |  | 39 | 2 | 38 | 39.5 | 536008.198 | -0.162 |
| 40 | 0 | 40 | 39.5 |  | 39 | 0 | 39 | 38.5 | 536051.892 | -0.005 |
| 40 | 0 | 40 | 40.5 |  | 39 | 0 | 39 | 39.5 | 536129.636 | 0.048 |
| 40 | 2 | 38 | 39.5 |  | 39 | 2 | 37 | 38.5 | 536257.468 | -0.257 |
| 40 | 2 | 38 | 40.5 |  | 39 | 2 | 37 | 39.5 | 536329.514 | -0.102 |
| 40 | 1 | 39 | 39.5 |  | 39 | 1 | 38 | 38.5 | 538787.509 | -0.050 |
| 40 | 1 | 39 | 40.5 |  | 39 | 1 | 38 | 39.5 | 538855.606 | 0.127 |

a) $\operatorname{In} \mathrm{MHz}$.

Table S2. Complete List of $\mathrm{SrND}_{2}$ Rotational Transition Frequencies ${ }^{\text {a }}$

| $\mathrm{N}^{\circ}$ | $K_{\text {a }}{ }^{\text {b }}$ | $\mathrm{K}_{6}{ }^{\text {a }}$ | J | \& $\mathrm{N}^{\prime \prime}$ | $\mathrm{K}_{\mathrm{a}}^{\text {in }}$ | $\mathrm{K}_{0}{ }^{\text {² }}$ | $J^{18}$ | $V_{\text {obs }}$ | $V_{\text {obs - calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 31 | 6 | 25 | 30.5 | 30 | 6 | 24 | 29.5 | 352281.782 | -0.083 |
| 31 | 6 | 26 | 30.5 | 30 | 6 | 25 | 29.5 | 352281.782 | -0.083 |
| 31 | 6 | 25 | 31.5 | 30 | 6 | 24 | 30.5 | 352344.764 | 0.050 |
| 31 | 6 | 26 | 31.5 | 30 | 6 | 25 | 30.5 | 352344.764 | 0.050 |
| 32 | 6 | 26 | 31.5 | 31 | 6 | 25 | 30.5 | 363620.374 | -0.045 |
| 32 | 6 | 27 | 31.5 | 31 | 6 | 26 | 30.5 | 363620.374 | -0.045 |
| 32 | 6 | 26 | 32.5 | 31 | 6 | 25 | 31.5 | 363683.362 | 0.052 |
| 32 | 6 | 27 | 32.5 | 31 | 6 | 26 | 31.5 | 363683.362 | 0.052 |
| 32 | 5 | 27 | 31.5 | 31 | 5 | 26 | 30.5 | 364351.033 | -0.061 |
| 32 | 5 | 28 | 31.5 | 31 | 5 | 27 | 30.5 | 364351.033 | -0.060 |
| 32 | 5 | 27 | 32.5 | 31 | 5 | 26 | 31.5 | 364414.280 | 0.002 |
| 32 | 5 | 28 | 32.5 | 31 | 5 | 27 | 31.5 | 364414.280 | 0.003 |
| 32 | 4 | 28 | 31.5 | 31 | 4 | 27 | 30.5 | 364927.557 | -0.018 |
| 32 | 4 | 29 | 31.5 | 31 | 4 | 28 | 30.5 | 364927.557 | 0.098 |
| 32 | 4 | 28 | 32.5 | 31 | 4 | 27 | 31.5 | 364990.887 | -0.044 |
| 32 | 4 | 29 | 32.5 | 31 | 4 | 28 | 31.5 | 364990.887 | 0.070 |
| 32 | 2 | 31 | 31.5 | 31 | 2 | 30 | 30.5 | 365479.587 | 0.048 |
| 32 | 2 | 31 | 32.5 | 31 | 2 | 30 | 31.5 | 365544.460 | 0.091 |
| 32 | 2 | 30 | 31.5 | 31 | 2 | 29 | 30.5 | 366162.405 | -0.037 |
| 32 | 2 | 30 | 32.5 | 31 | 2 | 29 | 31.5 | 366222.641 | -0.114 |
| 33 | 6 | 27 | 32.5 | 32 | 6 | 26 | 31.5 | 374956.416 | -0.019 |
| 33 | 6 | 28 | 32.5 | 32 | 6 | 27 | 31.5 | 374956.416 | -0.019 |
| 33 | 6 | 27 | 33.5 | 32 | 6 | 26 | 32.5 | 375019.356 | -0.007 |
| 33 | 6 | 28 | 33.5 | 32 | 6 | 27 | 32.5 | 375019.356 | -0.007 |
| 33 | 4 | 29 | 32.5 | 32 | 4 | 28 | 31.5 | 376302.617 | -0.086 |
| 33 | 4 | 30 | 32.5 | 32 | 4 | 29 | 31.5 | 376302.617 | 0.058 |
| 33 | 4 | 29 | 33.5 | 32 | 4 | 28 | 32.5 | 376366.004 | -0.054 |
| 33 | 4 | 30 | 33.5 | 32 | 4 | 29 | 32.5 | 376366.004 | 0.087 |
| 33 | 2 | 31 | 32.5 | 32 | 2 | 30 | 31.5 | 377607.401 | -0.030 |
| 33 | 2 | 31 | 33.5 | 32 | 2 | 30 | 32.5 | 377667.436 | -0.094 |
| 34 | 1 | 34 | 33.5 | 33 | 1 | 33 | 32.5 | 385267.076 | 0.036 |
| 34 | 1 | 34 | 34.5 | 33 | 1 | 33 | 33.5 | 385338.623 | -0.103 |
| 34 | 6 | 28 | 33.5 | 33 | 6 | 27 | 32.5 | 386289.837 | 0.006 |
| 34 | 6 | 29 | 33.5 | 33 | 6 | 28 | 32.5 | 386289.837 | 0.006 |
| 34 | 6 | 28 | 34.5 | 33 | 6 | 27 | 33.5 | 386352.796 | 0.008 |
| 34 | 6 | 29 | 34.5 | 33 | 6 | 28 | 33.5 | 386352.796 | 0.008 |
| 34 | 4 | 30 | 33.5 | 33 | 4 | 29 | 32.5 | 387675.026 | -0.040 |
| 34 | 4 | 31 | 33.5 | 33 | 4 | 30 | 32.5 | 387675.026 | 0.138 |
| 34 | 4 | 30 | 34.5 | 33 | 4 | 29 | 33.5 | 387738.359 | -0.059 |
| 34 | 4 | 31 | 34.5 | 33 | 4 | 30 | 33.5 | 387738.359 | 0.116 |
| 34 | 0 | 34 | 33.5 | 33 | 0 | 33 | 32.5 | 387766.045 | -0.029 |
| 34 | 0 | 34 | 34.5 | 33 | 0 | 33 | 33.5 | 387835.323 | 0.004 |
| 34 | 3 | 32 | 33.5 | 33 | 3 | 31 | 32.5 | 388156.559 | -0.054 |
| 34 | 3 | 31 | 33.5 | 33 | 3 | 30 | 32.5 | 388176.524 | 0.116 |
| 34 | 3 | 32 | 34.5 | 33 | 3 | 31 | 33.5 | 388219.872 | -0.104 |
| 34 | 3 | 31 | 34.5 | 33 | 3 | 30 | 33.5 | 388239.542 | -0.012 |
| 34 | 2 | 33 | 33.5 | 33 | 2 | 32 | 32.5 | 388236.656 | 0.065 |
| 34 | 2 | 33 | 34.5 | 33 | 2 | 32 | 33.5 | 388301.517 | -0.013 |
| 34 | 2 | 32 | 33.5 | 33 | 2 | 31 | 32.5 | 389052.258 | -0.021 |

Table S2. Cont'd.

| $\mathrm{N}^{+}$ | $K_{a}{ }^{\prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {² }}$ | J | $\leftarrow \quad \mathrm{N}^{\prime \prime}$ | $\mathrm{K}_{\mathrm{s}}{ }^{\text {²}}$ | $K_{c}^{\prime \prime}$ | $\mathrm{J}^{\prime \prime}$ | $V_{\text {obs }}$ | $\nu_{\text {obs -calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 34 | 2 | 32 | 34.5 | 33 | 2 | 31 | 33.5 | 389112.114 | -0.046 |
| 34 | 1 | 33 | 33.5 | 33 | 1 | 32 | 32.5 | 391400.004 | 0.066 |
| 34 | 1 | 33 | 34.5 | 33 | 1 | 32 | 33.5 | 391459.132 | -0.051 |
| 35 | 1 | 35 | 34.5 | 34 | 1 | 34 | 33.5 | 396549.787 | -0.017 |
| 35 | 1 | 35 | 35.5 | 34 | 1 | 34 | 34.5 | 396621.539 | -0.017 |
| 35 | 6 | 29 | 34.5 | 34 | 6 | 28 | 33.5 | 397620.540 | 0.019 |
| 35 | 6 | 30 | 34.5 | 34 | 6 | 29 | 33.5 | 397620.540 | 0.019 |
| 35 | 6 | 29 | 35.5 | 34 | 6 | 28 | 34.5 | 397683.510 | 0.007 |
| 35 | 6 | 30 | 35.5 | 34 | 6 | 29 | 34.5 | 397683.510 | 0.007 |
| 35 | 5 | 30 | 34.5 | 34 | 5 | 29 | 33.5 | 398415.019 | -0.008 |
| 35 | 5 | 31 | 34.5 | 34 | 5 | 30 | 33.5 | 398415.019 | -0.007 |
| 35 | 5 | 30 | 35.5 | 34 | 5 | 29 | 34.5 | 398478.235 | -0.019 |
| 35 | 5 | 31 | 35.5 | 34 | 5 | 30 | 34.5 | 398478.235 | -0.018 |
| 35 | 0 | 35 | 34.5 | 34 | 0 | 34 | 33.5 | 399082.698 | -0.008 |
| 35 | 0 | 35 | 35.5 | 34 | 0 | 34 | 34.5 | 399152.159 | -0.071 |
| 35 | 2 | 34 | 34.5 | 34 | 2 | 33 | 33.5 | 399609.273 | 0.054 |
| 35 | 2 | 34 | 35.5 | 34 | 2 | 33 | 34.5 | 399674.171 | -0.044 |
| 35 | 2 | 33 | 34.5 | 34 | 2 | 32 | 33.5 | 400496.944 | 0.017 |
| 35 | 2 | 33 | 35.5 | 34 | 2 | 32 | 34.5 | 400556.495 | -0.090 |
| 35 | 1 | 34 | 34.5 | 34 | 1 | 33 | 33.5 | 402857.100 | 0.086 |
| 35 | 1 | 34 | 35.5 | 34 | 1 | 33 | 34.5 | 402916.305 | -0.047 |
| 36 | 6 | 30 | 35.5 | 35 | 6 | 29 | 34.5 | 408948.432 | 0.012 |
| 36 | 6 | 31 | 35.5 | 35 | 6 | 30 | 34.5 | 408948.432 | 0.012 |
| 36 | 6 | 30 | 36.5 | 35 | 6 | 29 | 35.5 | 409011.401 | -0.022 |
| 36 | 6 | 31 | 36.5 | 35 | 6 | 30 | 35.5 | 409011.401 | -0.022 |
| 36 | 5 | 31 | 35.5 | 35 | 5 | 30 | 34.5 | 409763.978 | 0.025 |
| 36 | 5 | 32 | 35.5 | 35 | 5 | 31 | 34.5 | 409763.978 | 0.026 |
| 36 | 5 | 31 | 36.5 | 35 | 5 | 30 | 35.5 | 409827.179 | -0.008 |
| 36 | 5 | 32 | 36.5 | 35 | 5 | 31 | 35.5 | 409827.179 | -0.007 |
| 39 | 1 | 39 | 38.5 | 38 | 1 | 38 | 37.5 | 441637.468 | 0.060 |
| 39 | 1 | 39 | 39.5 | 38 | 1 | 38 | 38.5 | 441709.431 | -0.005 |
| 39 | 6 | 33 | 38.5 | 38 | 6 | 32 | 37.5 | 442914.572 | 0.055 |
| 39 | 6 | 34 | 38.5 | 38 | 6 | 33 | 37.5 | 442914.572 | 0.055 |
| 39 | 6 | 33 | 39.5 | 38 | 6 | 32 | 38.5 | 442977.520 | -0.037 |
| 39 | 6 | 34 | 39.5 | 38 | 6 | 33 | 38.5 | 442977.520 | -0.037 |
| 39 | 5 | 34 | 38.5 | 38 | 5 | 33 | 37.5 | 443792.391 | 0.035 |
| 39 | 5 | 35 | 38.5 | 38 | 5 | 34 | 37.5 | 443792.391 | 0.038 |
| 39 | 5 | 34 | 39.5 | 38 | 5 | 33 | 38.5 | 443855.502 | -0.092 |
| 39 | 5 | 35 | 39.5 | 38 | 5 | 34 | 38.5 | 443855.502 | -0.089 |
| 39 | 4 | 35 | 38.5 | 38 | 4 | 34 | 37.5 | 444492.233 | -0.181 |
| 39 | 4 | 36 | 38.5 | 38 | 4 | 35 | 37.5 | 444492.233 | 0.284 |
| 39 | 4 | 35 | 39.5 | 38 | 4 | 34 | 38.5 | 444555.485 | -0.227 |
| 39 | 4 | 36 | 39.5 | 38 | 4 | 35 | 38.5 | 444555.485 | 0.232 |
| 39 | 0 | 39 | 38.5 | 38 | 0 | 38 | 37.5 | 444273.899 | 0.051 |
| 39 | 0 | 39 | 39.5 | 38 | 0 | 38 | 38.5 | 444344.548 | 0.027 |
| 39 | 2 | 38 | 38.5 | 38 | 2 | 37 | 37.5 | 445057.748 | 0.051 |
| 39 | 2 | 38 | 39.5 | 38 | 2 | 37 | 38.5 | 445122.905 | -0.024 |
| 39 | 2 | 37 | 38.5 | 38 | 2 | 36 | 37.5 | 446272.059 | -0.007 |
| 39 | 2 | 37 | 39.5 | 38 | 2 | 36 | 38.5 | 446330.866 | 0.050 |

Table S2. Cont'd.

| $\mathrm{N}^{\mathrm{j}}$ | $\mathbf{K}_{\mathbf{a}}{ }^{\text {a }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | J' | $\leftarrow$ | $\mathrm{N}^{\mathrm{m}}$ | $\mathrm{K}_{\mathrm{a}}{ }^{\text {m }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {P }}$ | $J^{3}$ | $V_{\text {obs }}$ | $\nu_{\text {obs-cale }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 39 | 3 | 37 | 38.5 |  | 38 | 3 | 36 | 37.5 | 445047.596 | -0.008 |
| 39 | 3 | 36 | 38.5 |  | 38 | 3 | 35 | 37.5 | 445086.908 | 0.063 |
| 39 | 3 | 37 | 39.5 |  | 38 | 3 | 36 | 38.5 | 445110.800 | -0.068 |
| 39 | 3 | 36 | 39.5 |  | 38 | 3 | 35 | 38.5 | 445149.762 | 0.027 |
| 39 | 1 | 38 | 38.5 |  | 38 | 1 | 37 | 37.5 | 448634.882 | 0.055 |
| 39 | 1 | 38 | 39.5 |  | 38 | 1 | 37 | 38.5 | 448694.576 | 0.004 |
| 40 | 1 | 40 | 39.5 |  | 39 | 1 | 39 | 38.5 | 452897.952 | 0.047 |
| 40 | 1 | 40 | 40.5 |  | 39 | 1 | 39 | 39.5 | 452970.035 | 0.030 |
| 40 | 6 | 34 | 39.5 |  | 39 | 6 | 33 | 38.5 | 454230.515 | 0.121 |
| 40 | 6 | 35 | 39.5 |  | 39 | 6 | 34 | 38.5 | 454230.515 | 0.121 |
| 40 | 6 | 34 | 40.5 |  | 39 | 6 | 33 | 39.5 | 454293.433 | -0.008 |
| 40 | 6 | 35 | 40.5 |  | 39 | 6 | 34 | 39.5 | 454293.433 . | -0.008 |
| 40 | 5 | 35 | 39.5 |  | 39 | 5 | 34 | 38.5 | 455128.800 | 0.060 |
| 40 | 5 | 36 | 39.5 |  | 39 | 5 | 35 | 38.5 | 455128.800 | 0.063 |
| 40 | 5 | 35 | 40.5 |  | 39 | 5 | 34 | 39.5 | 455191.965 | -0.010 |
| 40 | 5 | 36 | 40.5 |  | 39 | 5 | 35 | 39.5 | 455191.965 | -0.006 |
| 40 | 4 | 36 | 39.5 |  | 39 | 4 | 35 | 38.5 | 455846.180 | -0.210 |
| 40 | 4 | 37 | 39.5 |  | 39 | 4 | 36 | 38.5 | 455846.180 | 0.347 |
| 40 | 4 | 36 | 40.5 |  | 39 | 4 | 35 | 39.5 | 455909.407 | -0.263 |
| 40 | 4 | 37 | 40.5 |  | 39 | 4 | 36 | 39.5 | 455909.407 | 0.286 |
| 40 | 0 | 40 | 39.5 |  | 39 | 0 | 39 | 38.5 | 455552.165 | 0.038 |
| 40 | 0 | 40 | 40.5 |  | 39 | 0 | 39 | 39.5 | 455623.133 | 0.040 |
| 40 | 2 | 39 | 39.5 |  | 39 | 2 | 38 | 38.5 | 456408.744 | 0.017 |
| 40 | 3 | 38 | 39.5 |  | 39 | 3 | 37 | 38.5 | 456416.111 | -0.047 |
| 40 | 3 | 37 | 39.5 |  | 39 | 3 | 36 | 38.5 | 456460.708 | 0.033 |
| 40 | 2 | 39 | 40.5 |  | 39 | 2 | 38 | 39.5 | 456473.983 | -0.038 |
| 40 | 3 | 38 | 40.5 |  | 39 | 3 | 37 | 39.5 | 456479.328 | -0.073 |
| 40 | 3 | 37 | 40.5 |  | 39 | 3 | 36 | 39.5 | 456523.535 | 0.032 |
| 40 | 2 | 38 | 39.5 |  | 39 | 2 | 37 | 38.5 | 457714.563 | 0.006 |
| 40 | 2 | 38 | 40.5 |  | 39 | 2 | 37 | 39.5 | 457773.074 | -0.002 |
| 40 | 1 | 39 | 39.5 |  | 39 | 1 | 38 | 38.5 | 460065.916 | 0.013 |
| 40 | 1 | 39 | 40.5 |  | 39 | 1 | 38 | 39.5 | 460125.894 | 0.135 |
| 41 | 1 | 41 | 40.5 |  | 40 | 1 | 40 | 39.5 | 464153.684 | 0.056 |
| 41 | 1 | 41 | 41.5 |  | 40 | 1 | 40 | 40.5 | 464225.832 | 0.032 |
| 41 | 6 | 35 | 40.5 |  | 40 | 6 | 34 | 39.5 | 465543.086 | 0.037 |
| 41 | 6 | 36 | 40.5 |  | 40 | 6 | 35 | 39.5 | 465543.086 | 0.037 |
| 41 | 6 | 35 | 41.5 |  | 40 | 6 | 34 | 40.5 | 465606.021 | -0.078 |
| 41 | 6 | 36 | 41.5 |  | 40 | 6 | 35 | 40.5 | 465606.021 | -0.078 |
| 41 | 5 | 36 | 40.5 |  | 40 | 5 | 35 | 39.5 | 466461.823 | 0.053 |
| 41 | 5 | 37 | 40.5 |  | 40 | 5 | 36 | 39.5 | 466461.823 | 0.058 |
| 41 | 5 | 36 | 41.5 |  | 40 | 5 | 35 | 40.5 | 466525.039 | 0.041 |
| 41 | 5 | 37 | 41.5 |  | 40 | 5 | 36 | 40.5 | 466525.039 | 0.045 |
| 41 | 4 | 37 | 40.5 |  | 40 | 4 | 36 | 39.5 | 467196.707 | -0.293 |
| 41 | 4 | 38 | 40.5 |  | 40 | 4 | 37 | 39.5 | 467196.707 | 0.369 |
| 41 | 4 | 37 | 41.5 |  | 40 | 4 | 36 | 40.5 | 467259.956 | -0.305 |
| 41 | 4 | 38 | 41.5 |  | 40 | 4 | 37 | 40.5 | 467259.956 | 0.348 |
| 41 | 0 | 41 | 40.5 |  | 40 | 0 | 40 | 39.5 | 466822.376 | 0.005 |
| 41 | 0 | 41 | 41.5 |  | 40 | 0 | 40 | 40.5 | 466893.655 | 0.024 |
| 41 | 2 | 40 | 40.5 |  | 40 | 2 | 39 | 39.5 | 467755.078 | -0.012 |

Table S2. Cont'd.

| N | $\mathrm{K}_{\mathrm{a}}{ }^{\text {a }}$ | $K_{c}{ }^{\prime}$ | J | $\leftarrow$ | $\mathrm{N}^{\text {m }}$ | $\mathrm{K}^{\text {a }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $J^{31}$ | $V_{\text {obs }}$ | $V_{\text {obs-cale }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 41 | 3 | 39 | 40.5 |  | 40 | 3 | 38 | 39.5 | 467781.174 | -0.093 |
| 41 | 2 | 40 | 41.5 |  | 40 | 2 | 39 | 40.5 | 467820.402 | -0.045 |
| 41 | 3 | 38 | 40.5 |  | 40 | 3 | 37 | 39.5 | 467831.646 | 0.039 |
| 41 | 3 | 39 | 41.5 |  | 40 | 3 | 38 | 40.5 | 467844.397 | -0.090 |
| 41 | 3 | 38 | 41.5 |  | 40 | 3 | 37 | 40.5 | 467894.412 | 0.042 |
| 41 | 2 | 39 | 40.5 |  | 40 | 2 | 38 | 39.5 | 469156.334 | 0.008 |
| 41 | 2 | 39 | 41.5 |  | 40 | 2 | 38 | 40.5 | 469214.640 | 0.025 |
| 41 | 1 | 40 | 40.5 |  | 40 | 1 | 39 | 39.5 | 471491.346 | 0.024 |
| 41 | 1 | 40 | 41.5 |  | 40 | 1 | 39 | 40.5 | 471551.307 | 0.013 |
| 42 | 1 | 42 | 41.5 |  | 41 | 1 | 41 | 40.5 | 475404.526 | 0.055 |
| 42 | 1 | 42 | 42.5 |  | 41 | 1 | 41 | 41.5 | 475476.775 | 0.060 |
| 42 | 6 | 36 | 41.5 |  | 41 | 6 | 35 | 40.5 | 476852.359 | -0.036 |
| 42 | 6 | 37 | 41.5 |  | 41 | 6 | 36 | 40.5 | 476852.359 | -0.036 |
| 42 | 6 | 36 | 42.5 |  | 41 | 6 | 35 | 41.5 | 476915.563 | 0.119 |
| 42 | 6 | 37 | 42.5 |  | 41 | 6 | 36 | 41.5 | 476915.563 | 0.119 |
| 42 | 5 | 37 | 41.5 |  | 41 | 5 | 36 | 40.5 | 477791.143 | -0.213 |
| 42 | 5 | 38 | 41.5 |  | 41 | 5 | 37 | 40.5 | 477791.143 | -0.208 |
| 42 | 5 | 37 | 42.5 |  | 41 | 5 | 36 | 41.5 | 477854.619 | 0.042 |
| 42 | 5 | 38 | 42.5 |  | 41 | 5 | 37 | 41.5 | 477854.619 | 0.048 |
| 42 | 0 | 42 | 41.5 |  | 41 | 0 | 41 | 40.5 | 478084.051 | -0.426 |
| 42 | 0 | 42 | 42.5 |  | 41 | 0 | 41 | 41.5 | 478156.080 | 0.048 |
| 42 | 4 | 38 | 41.5 |  | 41 | 4 | 37 | 40.5 | 478543.861 | -0.298 |
| 42 | 4 | 39 | 41.5 |  | 41 | 4 | 38 | 40.5 | 478543.861 | 0.486 |
| 42 | 4 | 38 | 42.5 |  | 41 | 4 | 37 | 41.5 | 478607.027 | -0.371 |
| 42 | 4 | 39 | 42.5 |  | 41 | 4 | 38 | 41.5 | 478607.027 | 0.402 |
| 42 | 2 | 41 | 41.5 |  | 41 | 2 | 40 | 40.5 | 479096.641 | -0.028 |
| 42 | 2 | 41 | 42.5 |  | 41 | 2 | 40 | 41.5 | 479162.033 | -0.058 |
| 42 | 2 | 40 | 41.5 |  | 41 | 2 | 39 | 40.5 | 480597.233 | -0.023 |
| 42 | 2 | 40 | 42.5 |  | 41 | 2 | 39 | 41.5 | 480655.344 | 0.027 |
| 42 | 1 | 41 | 41.5 |  | 41 | 1 | 40 | 40.5 | 482910.932 | $<0.000$ |
| 42 | 1 | 41 | 42.5 |  | 41 | 1 | 40 | 41.5 | 482971.038 | 0.016 |
| 43 | 1 | 43 | 42.5 |  | 42 | 1 | 42 | 41.5 | 486650.391 | 0.061 |
| 43 | 1 | 43 | 43.5 |  | 42 | 1 | 42 | 42.5 | 486722.702 | 0.055 |
| 43 | 6 | 37 | 42.5 |  | 42 | 6 | 36 | 41.5 | 488158.358 | 0.016 |
| 43 | 6 | 38 | 42.5 |  | 42 | 6 | 37 | 41.5 | 488158.358 | 0.016 |
| 43 | 6 | 37 | 43.5 |  | 42 | 6 | 36 | 42.5 | 488221.296 | -0.093 |
| 43 | 6 | 38 | 43.5 |  | 42 | 6 | 37 | 42.5 | 488221.296 | -0.093 |
| 43 | 5 | 38 | 42.5 |  | 42 | 5 | 37 | 41.5 | 489117.547 | 0.136 |
| 43 | 5 | 39 | 42.5 |  | 42 | 5 | 38 | 41.5 | 489117.547 | 0.143 |
| 43 | 5 | 38 | 43.5 |  | 42 | 5 | 37 | 42.5 | 489180.624 | 0.003 |
| 43 | 5 | 39 | 43.5 |  | 42 | 5 | 38 | 42.5 | 489180.624 | 0.010 |
| 43 | 0 | 43 | 42.5 |  | 42 | 0 | 42 | 41.5 | 489338.396 | 0.041 |
| 43 | 0 | 43 | 43.5 |  | 42 | 0 | 42 | 42.5 | 489410.290 | 0.086 |
| 43 | 4 | 40 | 42.5 |  | 42 | 4 | 39 | 41.5 | 489886.921 | 0.067 |
| 43 | 4 | 39 | 42.5 |  | 42 | 4 | 38 | 41.5 | 489887.528 | -0.251 |
| 43 | 4 | 40 | 43.5 |  | 42 | 4 | 39 | 42.5 | 489950.111 | 0.028 |
| 43 | 4 | 39 | 43.5 |  | 42 | 4 | 38 | 42.5 | 489950.861 | -0.135 |
| 43 | 2 | 42 | 42.5 |  | 42 | 2 | 41 | 41.5 | 490433.258 | -0.092 |
| 43 | 2 | 42 | 43.5 |  | 42 | 2 | 41 | 42.5 | 490498.737 | -0.100 |

Table S2. Cont'd.

| $\mathrm{N}^{\circ}$ | $K_{8}{ }^{\text {b }}$ | $K_{\text {c }}{ }^{\text {a }}$ | J | $\leftarrow$ | $\mathrm{N}^{\prime \prime}$ | $\mathrm{K}_{\mathrm{e}}{ }^{\text {² }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $\mathrm{J}^{19}$ | $V_{\text {obs }}$ | $V_{\text {obs -calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 43 | 2 | 41 | 42.5 |  | 42 | 2 | 40 | 41.5 | 492037.234 | 0.013 |
| 43 | 2 | 41 | 43.5 |  | 42 | 2 | 40 | 42.5 | 492095.129 | 0.075 |
| 43 | 1 | 42 | 42.5 |  | 42 | 1 | 41 | 41.5 | 494324.534 | -0.043 |
| 43 | 1 | 42 | 43.5 |  | 42 | 1 | 41 | 42.5 | 494384.784 | -0.005 |
| 44 | 1 | 44 | 43.5 |  | 43 | 1 | 43 | 42.5 | 497891.101 | <0.000 |
| 44 | 1 | 44 | 44.5 |  | 43 | 1 | 43 | 43.5 | 497963.532 | 0.039 |
| 44 | 6 | 38 | 43.5 |  | 43 | 6 | 37 | 42.5 | 499460.813 | 0.011 |
| 44 | 6 | 39 | 43.5 |  | 43 | 6 | 38 | 42.5 | 499460.813 | 0.012 |
| 44 | 6 | 38 | 44.5 |  | 43 | 6 | 37 | 43.5 | 499523.794 | -0.050 |
| 44 | 6 | 39 | 44.5 |  | 43 | 6 | 38 | 43.5 | 499523.794 | -0.050 |
| 44 | 5 | 39 | 43.5 |  | 43 | 5 | 38 | 42.5 | 500439.813 | -0.031 |
| 44 | 5 | 40 | 43.5 |  | 43 | 5 | 39 | 42.5 | 500439.813 | -0.022 |
| 44 | 5 | 39 | 44.5 |  | 43 | 5 | 38 | 43.5 | 500503.101 | 0.059 |
| 44 | 5 | 40 | 44.5 |  | 43 | 5 | 39 | 43.5 | 500503.101 | 0.067 |
| 44 | 0 | 44 | 43.5 |  | 43 | 0 | 43 | 42.5 | 500583.903 | -0.021 |
| 44 | 0 | 44 | 44.5 |  | 43 | 0 | 43 | 43.5 | 500656.100 | 0.034 |
| 44 | 2 | 43 | 43.5 |  | 43 | 2 | 42 | 42.5 | 501764.875 | -0.140 |
| 44 | 2 | 43 | 44.5 |  | 43 | 2 | 42 | 43.5 | 501830.423 | -0.146 |
| 44 | 3 | 42 | 43.5 |  | 43 | 3 | 41 | 42.5 | 501855.222 | 0.320 |
| 44 | 3 | 42 | 44.5 |  | 43 | 3 | 41 | 43.5 | 501918.222 | 0.167 |
| 44 | 3 | 41 | 44.5 |  | 43 | 3 | 40 | 43.5 | 501989.020 | 0.045 |
| 44 | 2 | 42 | 43.5 |  | 43 | 2 | 41 | 42.5 | 503476.055 | -0.028 |
| 44 | 2 | 42 | 44.5 |  | 43 | 2 | 41 | 43.5 | 503533.729 | 0.038 |
| 45 | 6 | 39 | 44.5 |  | 44 | 6 | 38 | 43.5 | 510759.680 | -0.005 |
| 45 | 6 | 40 | 44.5 |  | 44 | 6 | 39 | 43.5 | 510759.680 | -0.005 |
| 45 | 6 | 39 | 45.5 |  | 44 | 6 | 38 | 44.5 | 510822.668 | -0.053 |
| 45 | 6 | 40 | 45.5 |  | 44 | 6 | 39 | 44.5 | 510822.668 | -0.053 |
| 45 | 5 | 40 | 44.5 |  | 44 | 5 | 39 | 43.5 | 511758.054 | -0.513 |
| 45 | 5 | 41 | 44.5 |  | 44 | 5 | 40 | 43.5 | 511758.054 | -0.502 |
| 45 | 0 | 45 | 45.5 |  | 44 | 0 | 44 | 44.5 | 511893.535 | -0.010 |
| 45 | 2 | 44 | 45.5 |  | 44 | 2 | 43 | 44.5 | 513156.953 | -0.220 |
| 45 | 2 | 43 | 44.5 |  | 44 | 2 | 42 | 43.5 | 514913.660 | -0.035 |
| 45 | 2 | 43 | 45.5 |  | 44 | 2 | 42 | 44.5 | 514971.165 | 0.083 |
| 46 | 1 | 46 | 45.5 |  | 45 | 1 | 45 | 44.5 | 520356.902 | -0.074 |
| 46 | 1 | 46 | 46.5 |  | 45 | 1 | 45 | 45.5 | 520429.448 | -0.069 |
| 46 | 6 | 40 | 45.5 |  | 45 | 6 | 39 | 44.5 | 522054.939 | 0.036 |
| 46 | 6 | 41 | 45.5 |  | 45 | 6 | 40 | 44.5 | 522054.939 | 0.036 |
| 46 | 6 | 40 | 46.5 |  | 45 | 6 | 39 | 45.5 | 522117.919 | -0.010 |
| 46 | 6 | 41 | 46.5 |  | 45 | 6 | 40 | 45.5 | 522117.919 | -0.010 |
| 46 | 5 | 41 | 45.5 |  | 45 | 5 | 40 | 44.5 | 523073.565 | 0.076 |
| 46 | 5 | 42 | 45.5 |  | 45 | 5 | 41 | 44.5 | 523073.565 | 0.089 |
| 46 | 5 | 41 | 46.5 |  | 45 | 5 | 40 | 45.5 | 523136.702 | 0.044 |
| 46 | 5 | 42 | 46.5 |  | 45 | 5 | 41 | 45.5 | 523136.702 | 0.057 |
| 46 | 0 | 46 | 45.5 |  | 45 | 0 | 45 | 44.5 | 523049.757 | -0.097 |
| 46 | 0 | 46 | 46.5 |  | 45 | 0 | 45 | 45.5 | 523122.613 | 0.034 |
| 46 | 4 | 43 | 45.5 |  | 45 | 4 | 42 | 44.5 | 523895.018 | -0.045 |
| 46 | 4 | 42 | 45.5 |  | 45 | 4 | 41 | 44.5 | 523896.534 | -0.014 |
| 46 | 4 | 43 | 46.5 |  | 45 | 4 | 42 | 45.5 | 523958.188 | -0.032 |
| 46 | 4 | 42 | 46.5 |  | 45 | 4 | 41 | 45.5 | 523959.707 | 0.020 |

Table S 2. Cont'd.

| N | $\mathrm{K}_{\mathbf{8}}{ }^{\text { }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text { }}$ | f | $\leftarrow$ | $\mathrm{N}^{\text {p/ }}$ | $\mathrm{K}_{\mathrm{a}}{ }^{\text {P }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {m }}$ | $J^{\prime \prime}$ | $V_{\text {obs }}$ | $\nu_{\text {obs -calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 46 | 2 | 45 | 45.5 |  | 45 | 2 | 44 | 44.5 | 524413.130 | 0.290 |
| 46 | 2 | 45 | 46.5 |  | 45 | 2 | 44 | 45.5 | 524478.717 | 0.185 |
| 46 | 2 | 44 | 45.5 |  | 45 | 2 | 43 | 44.5 | 526349.806 | -0.096 |
| 46 | 2 | 44 | 46.5 |  | 45 | 2 | 43 | 45.5 | 526407.079 | 0.009 |
| 47 | 6 | 41 | 46.5 |  | 46 | 6 | 40 | 45.5 | 533346.393 | 0.029 |
| 47 | 6 | 42 | 46.5 |  | 46 | 6 | 41 | 45.5 | 533346.393 | 0.029 |
| 47 | 6 | 41 | 47.5 |  | 46 | 6 | 40 | 46.5 | 533409.347 | -0.033 |
| 47 | 6 | 42 | 47.5 |  | 46 | 6 | 41 | 46.5 | 533409.347 | -0.033 |
| 47 | 5 | 42 | 46.5 |  | 46 | 5 | 41 | 45.5 | 534384.659 | 0.138 |
| 47 | 5 | 43 | 46.5 |  | 46 | 5 | 42 | 45.5 | 534384.659 | 0.154 |
| 47 | 5 | 42 | 47.5 |  | 46 | 5 | 41 | 46.5 | 534447.855 | 0.182 |
| 47 | 5 | 43 | 47.5 |  | 46 | 5 | 42 | 46.5 | 534447.855 | 0.198 |
| 47 | 4 | 44 | 46.5 |  | 46 | 4 | 43 | 45.5 | 535223.325 | -0.099 |
| 47 | 4 | 43 | 46.5 |  | 46 | 4 | 42 | 45.5 | 535225.072 | -0.079 |
| 47 | 2 | 45 | 46.5 |  | 46 | 2 | 44 | 45.5 | 537784.368 | -0.169 |
| 47 | 2 | 45 | 47.5 |  | 46 | 2 | 44 | 46.5 | 537841.554 | 0.063 |

a) $\operatorname{In} \mathrm{MHz}$

## APPENDIX C

TRENDS IN THE ALKALINE-EARTH AMIDE SERIES: THE MILLIMETRE-WAVE SPECTRUM OF $\mathrm{MgNH}_{2}$ AND $\mathrm{MgND}_{2}\left(\mathrm{X}^{2} \mathrm{~A}_{1}\right)$
P. M. Sheridan and L. M. Ziurys, Canadian J. Phys. 79, 409-421 (2001).

# Trends in the alkaline-earth amide series: The millimetre-wave spectrum of $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ ( $\tilde{X}^{2} \mathrm{~A}_{1}$ ) 

P.M. Sheridan and L.M. Ziurys

Abstract: The pure rotational spectra of $\mathrm{MgNH}_{2}\left(\tilde{\mathrm{X}}^{2} \mathrm{~A}_{1}\right)$ and its deuterium isotopomer have been recorded using millimetre/sub-millimetre wave direct absorption lechniques. Both species were synthesized by the reaction of magnesium vapor and either $\mathrm{NH}_{3}$ or $\mathrm{ND}_{3}$ in a de discharge. Twelve rotational iransitions were measured for $\mathrm{MgNH}_{3}$, and eight transitions were observed for MgND: both in the range $120-530 \mathrm{GHz}$. Asymmerry components with $K_{0}=0-5.7$, and sometimes 6 . were measured for nearly every transition. Rotational. centrifugal distontion. and spin-rotation parameters have been accurately determined for both molecules. as well as an $r_{0}$ structure for magnesium amide. The data indicate that $\mathrm{Mg} \mathrm{NH}_{2}$ is a pianar molecule with $\mathrm{C}_{2}$ symmerry, similar to $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$, and does not undergo inversion. However. there appears to be subtie differences between $\mathrm{MgNH}_{2}$ and its calcium and sronitim analogs. Magnesium amide, for example. has a significantly larger $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle than $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$. In addition. the spin-rotation constants indicate slighly more in-plane p character for the unpaired electron in this molecule relative to that in calcium or strontium amide. Such differences may result from more covalent character in the bonding of $\mathrm{MgNH}_{2}$ in comparison to the heovier alkaline-earth amide species.

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Résumé : Utilisant des techniques d'absorption directe dans le domaine millimérrique/submillimérique, nous avons enregistré le spectre de rotation du $\mathrm{MgNH}_{2}\left(\bar{X}^{2} \mathrm{~A}_{1}\right)$ ei de son isolopomère deutérié. Nous avons synthétisé les deux échantillons gràce à la réaction causée par une décharge électrique de dans un mélange contenant de la vapeur de maqnésium et soit du $\mathrm{NH}_{3}$. soil du ND. Nous avons mesuré douze iransitions robationnelles dans le $\mathrm{MgNH}_{2}$ ef huit dans le $\mathrm{MgND}_{2}$, ouses dans le dornaine $120-530 \mathrm{GHz}$. Presque chaque sransition monire une composante asymétrique avec $K_{n}=0-5,7$ et même 6 . Nous avons déterminé les paramètres rotationnel. centrifuge, de distorsion el de couplage spin-ronation pour les deux molécules. ainsi qu'une structure $r_{0}$ pour l'smidure de magnésium. Les données suggèrent que $\mathrm{MgNH}_{2}$ est une molécule plane à symérice $\mathrm{C}_{2 \mathrm{w}}$, semblable à $\mathrm{CaNH}_{2}$ el à $\mathrm{SriNH}_{\text {: }}$ et ne subit pas d'inversion. Il semble y avoir des différences subtiles enire le MgNH 2 et ses analogues Ca et Sr . L'amidure de magnésium. par exemple. a un angle de liaison $\mathrm{H}-\mathrm{N}-\mathrm{H}$ signiticativement plus grand. De plus. te couplage spin-rotation indique que l'élecrron planaire non pairé a une composante $p$ dans le

[^1]plan plus imponante dans MgNH 2 . Il esf possible que ces différences refètent une covariance plus marquée du lien dans le MgNH, que dans ses cousins alcalins plus lourds.

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## 1. Introduction

The bonding between monovalemt alkali and alkaline-earh metals with small ligands has been the subject of many theoretical and experimental investigations. Theoretically, Rinner [1] proposed one of the earliest quantitative models of such interactions, specifically for alkali halide species, interpreting them in the context of ion polarization. The polarization concept has been more recently exiended to characterize alkaline-earh halides as well. (e.g.. Field and Giitins [2]), including applications for ligand field theory (e.g. Rice et al. [3]). Ab inisio calculations have also been carried out for other small alkaline-earth species. for example by Oriz [4]. The basic conclusion of these theoretical investigations is that the bonding in simple alkali and alkaline-earth compounds can be areated as ionic. and various molecular properies can be accurately predicied making this assumption.

This ionic model has been supponed by experimental evidence. Numerous alkali and alkaline-earth compounds have been investigated by electronic and rotational spectroscopy (see ref. 5 for an overview). The isoelectronic alkaline-earth hydroxides and amides, in paricular. appear to follow an ionic bonding scheme. In fact. analyses of the electronic and rotational spectra of $\mathrm{CaOH}[6-8], \mathrm{SrOH}$ [9.10]. and $\mathrm{BaOH}[11.12]$ have shown that these molecules are tightly-bound linear species best represemted by an $\mathrm{M}^{+} \mathrm{OH}^{-}$configuration. Spectra of the low-lying electronic transitions of $\mathrm{CaNH} \mathrm{C}_{2}\left[13.141 . \mathrm{SrNH} \mathrm{N}_{2}\right.$ [15.16]. and $\mathrm{BaNH}_{2}$ [17] have also been recorded. Assignments of these data were based on similarities with spectra obsen'ed for the isoelectronic halide and hydroxide species. These alkaline-earth amides were determined to be planar with $\mathrm{C}_{2 \mathrm{v}}$ symmerry, suggestive of an $\mathrm{M}^{+} \mathrm{NH}_{2}{ }^{-}$sincture. No evidence of pyramidal geometry and (or) inversion was found, which would indicate covalent bonding as present in $\mathrm{NH}_{3}$. The planat siructure for $\mathrm{CaNH}_{2}$ and $\mathrm{SiNH}_{2}$ has recently been confinmed by pure rotational studies of these species conducted at high resolution in the millimetre-wave region [18.19].

At some level. however. small alkali and especially alkaline-eant compounds may begin to exhibit some covalent character to sheir bonding. This property should become apparent for the ligher metals of this class, such as Li. Be. and Mg. Unforwnately electronic mansitions of beryllium. magnesium, and lithium analogs of many metal species often lie outside the normal range of cw dye lasers. Consequenily, pure rotational studies of such compounds may be necessary to investigate their structure.

A good example of a molecule that represents a transition from ionic so covalent bonding is MgOH . As studies of its pure rotational spectrum have shown [20], this species is extremely floppy and appears to be quasilinear. Hence, the struciure of MgOH deviates from the strictly linear monohydroxide series.

Clearly it would be useful to study other Mg-bearing species so examine the interplay between these two extremes of metal-ligand bonds. One molecule of interest for this purpose is $\mathrm{MgNH}_{2}$. It can be conjectured that the $\mathrm{Mg}-\mathrm{N}$ bond will have some significant covalent character, which could lead to a pyramidal geometry and (or) inversion, as opposed to the planar $\mathrm{C}_{2 v}$ structure. MgNH2, however. has never been investigated by electronic spectroscopy, or any. other method. Hence. up to the presen. no structural information existed for this radical.

Currently in the Ziurys laborator; metal amide species are being investigated in their electronic ground states using gos-phase millimetre-wave techniques, including $\mathrm{CaNH}_{2}$ [18]. $\mathrm{SrNH}_{2}$ [19], $\mathrm{NaNH}_{2}$ [21], and $\mathrm{LiNH}_{2}$ [22]. Ver' recenlly, the pure rotational spectra of $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ have been recorded as well. Eighn to welve ransitions were measured for each species in multiple $\mathcal{K}_{0}$ components. (For $\mathrm{MgNH} \mathrm{H}_{2}$. some of the dara have already appeared in the astronomical liserature [23].) These spectra have been analyzed and rotational. centrifugal distorion. and fine structure parameters determined for both radicals. Here, we present our complete data set and analysis, including a discussion of the geomenic urends and bonding properies of the alkaline-eanth amide species.

## 2. Experimental

Measurements of the pure rotational spectra of $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ were conducted using one of the direct absorpion millimerre-wave spectromesers of the Ziurys group, details of which are available elsewhere [24]. To summarize, the insument consists of a unable millimetre-wave radiation source. a reaction chamber, and a detector. For this system, the radiation source consists of phase-locked Gunn oscillators and Schotthy-diode multipliers, which allow for near-continuous frequency coverage over the range $65-548 \mathrm{GHz}$. The radiation is lannched from a scalar feedhorn in a Gaussian-beam shape and quasi-optically propagated using teflon lenses and a polarizing grid through the reaction cell, which is a double-pass system. A Broida-type oven is anached to the cell for the production of metal vapor. The detector is an InSb bolometer, cooled to liquid-helium temperatures. The radiation source is frequency modulated at 25 kHz and detected at $2 f$.
$\mathrm{MgNH}_{2}$ was synthesized by the reaction of Mg vapor, seeded in argon carrier gas, and ammonia. The magnesium vapor was produced by a Broida-type oven, which was covered by a sieel plate with 2 cm diameter hole in the center to collimate the flow of magatesium vapor and preveni the coating of the rear lens of the cell. To acmally create this molecule, $10-15 \mathrm{mTorr}$ ( $1 \mathrm{Tont}=133.3 \mathrm{~Pa}$ ) of argon was allowed to flow into the vaporization region from the bottom of the oven to entrain the metal vapor. Approximately 10 mTort of ammonia was then added through a tube over the top of the oven. A de discharge was found necessary for the synthesis, using an electrode placed a few inches above the oven ( 1 inch $=2.54 \mathrm{~cm}$ ). Discharge conditions were typically $650-800 \mathrm{~mA}$ of current at 30 V , which resulted in the creation of a bright green plasma due to atomic emission of magnesium. For $\mathrm{MgND}_{2}$, the reaction conditions were the same except that 6 mTorr of $\mathrm{ND}_{3}$ was substituted for the ammonia.

Since no previous estimates of spectroscopic constants existed for either $\mathrm{MgNH}_{2}$ or $\mathrm{MgND}_{2}$, an extensive search had to be conducted for both molecules. On the order of $60-70 \mathrm{GHz}$ of frequency space was searched in 100 MHz intervals for both species. Once the specra were found and identified. actual frequency measurements were conducted. The final frequency determination of the lines was accomplished by laking an average of two 5 MHz scans, first in ascending, then in descending frequency. The resulting line profile was then fit with a Gaussian curve to establish the center frequency. For lines below 300 GHz , four to eight scans were necessary. For both molecules, linewidths varied from 350 to 1000 kHz over the frequency range $120-530 \mathrm{GHz}$.

## 3. Results

$\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ were found to be planar molecules belonging to the $\mathrm{C}_{2 v}$ point group. Thus, they can be classified as near-prolate asymmetric tops, bess described in a Hund's case (b) basis set. In this case. the quantum numbers are $N, J_{0} K_{a}$, and $K_{c} . N$ represents the rotational angular momentum of the molecule exclusive of nuclear and electron spin and $I$ indicates the fine structure interactions, where $J=N+S . K_{a}$ and $K_{c}$ are projections of $N$ onto the symmetry axis of the molecule in the respective prolate and oblate symmetric top limits. For asymmetric rop molecules, $K_{a}$ and $K_{c}$ are no longer welldefined quantum numbers since the asymmetry lifts the $K$ degeneracy. Therefore, $K_{a}$ and $K_{c}$ are used only as energy level labels. Moreover, the dipole moment lies along the $\hat{a}$-axis for alkaline-earth amide species. Consequently, the strongest electric-dipole allowed transitions obey the following selection rules: $\Delta N= \pm 1, \Delta J= \pm 1, \Delta K_{a}=0$, and $\Delta K_{c}= \pm 1$. Since $K_{a}$ does nor change, asymmerry componenis within each $N$ iransition can be labeled by the $K_{a}$ quanuum number.

Initially, 70 GHz of frequency space was scanned to establish the asymmetric top pattern for $\mathrm{MgNH}_{2}$. Since $\mathrm{MgNH}_{2}$ is a radical with one unpaired electron, fine structure resulis in the doubling of each $K_{a}$ component within every rotational transition. Slighty different spin-rotation splitings characterize individual $K_{a}$ components and subsequently this spliting was used to match such components over several transitions and establish their effective rotational constants. Assignment of the individual $K_{a}$ quantum numbers was then conducted, aided by the approximate $3: 1$ intensity ratios of ortho to para

Table 1. Selected transition frequencies of $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}\left(\overline{\mathrm{X}}^{2} \mathrm{~A}_{1}\right)^{\circ}$

| $N^{\prime}$ | $K_{a}{ }^{\prime}$ | $K_{r}{ }^{\prime}$ | $J^{\prime}$ | $N^{\prime \prime}$ | $K_{*}^{\prime \prime}$ | $K_{\text {r }}{ }^{\prime \prime}$ | $3^{\prime \prime}$ | $\mathrm{Mg}_{\mathrm{L}} \mathrm{H}_{2}$ |  | MgND |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $\nu_{\text {ots }}$ | $\nu_{\text {arimasa }}$ | $\nu_{\text {cbs }}$ | $\nu_{\text {ctr-cak }}$ |
| 5 | 1 | 5 | 4.5 | 4 | 1 | 4 | 3.5 | 129529.697 | -0.008 |  |  |
| 5 | 1 | 5 | 5.5 | 4 | 1 | 4 | 4.5 | 129568.688 | 0.010 |  |  |
| 5 | 1 | 4 | 4.5 | 4 | 1 | 3 | 3.5 | 131906.673 | 0.034 |  |  |
| 5 | 1 | 4 | 5.5 | 4 | 1 | 3 | 4.5 | 131946.543 | 0.021 |  |  |
| 6 | 1 | 6 | 5.5 | 5 | 1 | 5 | 4.5 | 155432.918 | $-0.030$ |  |  |
| 6 | 1 | 6 | 6.5 | 5 | 1 | 5 | 5.5 | 155471.705 | -0.027 |  |  |
| 6 | 1 | 5 | 5.5 | 5 | 1 | 4 | 4.5 | 158284.859 | -0.028 |  |  |
| 6 | 1 | 5 | 6.5 | 5 | 1 | 4 | 5.5 | 158324.558 | -0.023 |  |  |
| 9 | 1 | 9 | 8.5 | 8 | 1 | 8 | 7.5 | 233117.964 | -0.062 |  |  |
| 9 | 1 | 9 | 9.5 | 8 | 1 | 8 | 8.5 | 233156535 | -0.039 |  |  |
| 9 | 3 | 7 | 8.5 | 8 | 3 | 6 | 7.5 | 235005/777 | 0.021 |  | i |
| 9 | 3 | 6 | 8.5 | 8 | 3 | 5 | 7.5 | 235005.777 | -0.098 |  |  |
| 9 | 3 | 7 | 9.5 | 8 | 3 | 6 | 8.5 | 235046.269 | 0.061 |  |  |
| 9 | 3 | 6 | 9.5 | 8 | 3 | 5 | 8.5 | 235046.269 | -0.058 |  |  |
| 9 | 2 | 8 | 9.5 | 8 | 2 | 7 | 8.5 | 235199.672 | 0.114 |  |  |
| 9 | 2 | 7 | 8.5 | 8 | 2 | 6 | 7.5 | 235214.423 | -0.020 |  |  |
| 9 | 0 | 9 | 8.5 | 8 | 0 | 8 | 7.5 | 235247.037 | -0.003 |  |  |
| 9 | 2 | 7 | 9.5 | 8 | 2 | 6 | 8.5 | 235254.050 | 0.026 |  |  |
| 9 | 0 | 9 | 9.5 | 8 | 0 | 8 | 8.5 | 235285.788 | -0.049 |  |  |
| 9 | 1 | 8 | 8.5 | 8 | 1 | 7 | 7.5 | 237393.209 | 0.000 |  |  |
| 9 | 1 | 8 | 9.5 | 8 | 1 | 7 | 8.5 | 237432.665 | -0.003 |  |  |
| 19 | 1 | 19 | 18.5 | 18 | 1 | 18 | 17.5 | 491620.034 | 0.000 | 421079.641 | 0.005 |
| 19 | 1 | 19 | 19.5 | 18 | 1 | 18 | 18.5 | 491658.388 | -0.025 | 421112.475 | 0.011 |
| 19 | 7 | 13 | 18.5 | 18 | 7 | 12 | 17.5 | 492591.148 | 0.066 | 426065.593 | 0.001 |
| 19 | 7 | 13 | 19.5 | 18 | 7 | 12 | 18.5 | 492631.844 | -0.028 | 426101.913 | -0.016 |
| 19 | 7 | 12 | 18.5 | 18 | 7 | 11 | 17.5 | 492591.148 | 0.066 | 426065.593 | 0.001 |
| 19 | 7 | 12 | 19.5 | 18 | 7 | 11 | 18.5 | 492631.844 | -0.028 | 426101.913 | -0.016 |
| 19 | 6 | 14 | 18.5 | 18 | 6 | 13 | 17.5 |  |  | 426679.769 | 0.007 |
| 19 | 6 | 14 | 19.5 | 18 | 6 | 13 | 18.5 |  |  | 426715.338 | -0.026 |
| 19 | 6 | 13 | 18.5 | 18 | 6 | 12 | 17.5 |  |  | 426679.769 | 0.007 |
| 19 | 6 | 13 | 19.5 | 18 | 6 | 12 | 18.5 |  |  | 426715.338 | -0.026 |
| 19 | 5 | 15 | 18.5 | 18 | 5 | 14 | 17.5 | 494540.745 | 0.054 | 427206.702 | -0.051 |
| 19 | 5 | 15 | 19.5 | 18 | 5 | 14 | 18.5 | 494580.486 | -0.042 | 427241.674 | -0.062 |
| 19 | 5 | 14 | 18.5 | 18 | 5 | 13 | 17.5 | 494540.745 | 0.054 | 427206.702 | -0.056 |
| 19 | 5 | 14 | 19.5 | 18 | 5 | 13 | 18.5 | 494580.486 | -0.042 | 427241.674 | -0.067 |
| 19 | 4 | 16 | 18.5 | 18 | 4 | 15 | 17.5 | 495212.415 | 0.029 |  |  |
| 19 | 4 | 16 | 19.5 | 18 | 4 | 15 | 18.5 | 495251.820 | -0.048 |  |  |
| 19 | 4 | 15 | 18.5 | 18 | 4 | 14 | 17.5 | 495212.415 | 0.010 |  |  |
| 19 | 4 | 15 | 19.5 | 18 | 4 | 14 | 18.5 | 495251.820 | -0.067 |  |  |
| 19 | 3 | 17 | 18.5 | 18 | 3 | 16 | 17.5 | 495741.680 | 0.031 | 428077.169 | -0.095 |
| 19 | 3 | 17 | 19.5 | 18 | 3. | 16 | 18.5 | 495780.804 | -0.056 | 428111.290 | -0.082 |
| 19 | 3 | 16 | 18.5 | 18 | 3 | 15 | 17.5 | 495746.979 | 0.097 | 428148.859 | -0.050 |
| 19 | 3 | 16 | 19.5 | 18 | 3 | 15 | 18.5 | 495786.090 | -0.006 |  |  |
| 19 | 0 | 19 | 18.5 | 18 | 0 | 18 | 17.5 | 495787.733 | 0.102 | 425980.808 | -0.015 |
| 19 | 0 | 19 | 19.5 | 18 | 0 | 18 | 18.5 | 495826.273 | -0.031 | 426013.794 | 0.061 |
| 19 | 2 | 18 | 18.5 | 18 | 2 | 17 | 17.5 | 495950.841 | -0.001 | 427676.599 | 0.026 |
| 19 | 2 | 18 | 19.5 | 18 | 2 | 17 | 18.5 | 495989.785 | -0.022 | 427710.277 | 0.054 |
| 19 | 2 | 17 | 18.5 | 18 | 2 | 16 | 17.5 | 496464.383 | 0.015 | 429891.309 | -0.005 |
| 19 | 2 | 17 | 19.5 | 18 | 2 | 16 | 18.5 | 496503.481 | -0.012 |  |  |
| 19 | 1 | 18 | 18.5 | 18 | 1 | 17 | 17.5 | 509603.453 | 0.009 |  |  |

Table 1. (concluded.)

| $N^{\prime}$ | $X_{0}{ }^{\prime}$ | $K_{r}^{\prime}$ | $j$ | $N^{\prime \prime}$ | $K_{\text {K }}{ }^{\prime \prime}$ | $K_{r}{ }^{\prime \prime}$ | $j^{*}$ | $\mathrm{MgNH}_{3}$ <br> $v_{\mathrm{p} \times \mathrm{s}}$ | $\mathrm{MgND}_{2}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | $v_{\text {cha }}$-cak | $\psi_{\text {mas }}$ | $\nu_{\text {mis-rate }}$ |
| 19 | 1 | 18 | 19.5 | 18 | 1 | 17 | 18.5 | 500642.704 | -0.027 |  |  |
| 21 | 1 | 21 | 20.5 | 20 | 1 | 20 | 19.5 |  |  | 465193.666 | $-0.030$ |
| 21 | 1 | 21 | 21.5 | 20 | 1 | 20 | 20.5 |  |  | 465226.492 | 0.007 |
| 21 | 0 | 21 | 20.5 | 20 | 0 | 20 | 19.5 |  |  | 470214.794 | 0.018 |
| 21 | 0 | 21 | 21.5 | 20 | 0 | 20 | 20.5 |  |  | 470247.589 | 0.014 |
| 21 | 7 | 15 | 20.5 | 20 | 7 | 14 | 19.5 |  |  | 470837.862 | 0.037 |
| 21 | 7 | 15 | 21.5 | 20 | 7 | 14 | 20.5 |  |  | 470873.656 | -0.002 |
| 21 | 7 | 14 | 20.5 | 20 | 7 | 13 | 19.5 |  |  | 470837.862 | 0.037 |
| 21 | 7 | 14 | 21.5 | 20 | 7 | 13 | 20.5 | 1 |  | +70873.656 | $-0.002$ |
| 21 | 6 | 16 | 20.5 | 20 | 6 | 15 | 19.5 | , |  | +71519.023 | 0.018 |
| 21 | 6 | 16 | 21.5 | 20 | 6 | 15 | 20.5 | 1 |  | 471554.214 | -0.023 |
| 21 | 6 | 15 | 20.5 | 20 | 6 | 14 | 19.5 |  |  | 471519.023 | 0.018 |
| 21 | 6 | 15 | 21.5 | 20 | 6 | 14 | 20.5 |  |  | 471554.214 | -0.023 |
| 21 | 5 | 17 | 20.5 | 20 | 5 | 16 | 19.5 |  |  | +72107.195 | 0.008 |
| 21 | 5 | 17 | 21.5 | 20 | 5 | 16 | 20.5 |  |  | 472141.913 | -0.004 |
| 21 | 5 | 16 | 20.5 | 20 | 5 | 15 | 19.5 |  |  | +72107.195 | -0.005 |
| 21 | 5 | 16 | 21.5 | 20 | 5 | 15 | 20.5 |  |  | +72148.913 | -0.017 |
| 21 | 2 | 20 | 20.5 | 20 | 2 | 19 | 19.5 |  |  | 472509.300 | 0.038 |
| 21 | 2 | 20 | 21.5 | 20 | 2 | 19 | 20.5 |  |  | 472542.892 | 0.045 |
| 21 | 4 | 18 | 20.5 | 20 | 4 | 17 | 19.5 |  |  | +72627.702 | -0.049 |
| 21 | 4 | 18 | 21.5 | 20 | 4 | 17 | 20.5 |  |  | 472661.992 | -0.089 |
| 21 | 4 | 17 | 20.5 | 20 | 4 | 16 | 19.5 |  |  | +72629.588 | 0.094 |
| 21 | 4 | 17 | 21.5 | 20 | 4 | 16 | 20.5 |  |  | 172663.891 | 0.066 |
| 21 | 3 | 19 | 20.5 | 20 | 3 | 18 | 19.5 |  |  | +7309.4.829 | -0.058 |
| 21 | 3 | 19 | 21.5 | 20 | 3 | 18 | 20.5 |  |  | 473128.809 | $-0.103$ |
| 21 | 3 | 18 | 20.5 | 20 | 3 | 17 | 19.5 |  |  | \$73213.144 | 0.085 |
| 21 | 3 | 18 | 21.5 | 20 | 3 | 17 | 20.5 |  |  | 473247.229 | 0.093 |
| 21 | 2 | 19 | 20.5 | 20 | 2 | 18 | 19.5 |  |  | 475461.818 | 0.040 |
| 21 | 2 | 19 | 21.5 | 20 | 2 | 18 | 20.5 |  |  | 475496.040 | -0.052 |
| 21 | 1 | 20 | 20.5 | 20 | 1 | 19 | 19.5 |  |  | \$79561.08 ${ }^{\text {d }}$ | 0.034 |
| 21 | 1 | 20 | 21.5 | 20 | 1 | 19 | 20.5 |  |  | 479594.997 | -0.016 |

${ }^{\circ}$ In MHz.
levels due to nuclear spin statistics. Since the total wave function of the molecule must be antisymmeric upon a $C_{2}$ rotation or exchange of the protons, the rotational wave function changes symmery for $K_{a}$ even (or para) levels vs. $R_{a}$ odd (or ortho) levels. Also useful in assignment of $K_{a}$ quantum numbers was the comparison with the rotational spectum of $\mathrm{CaNH}_{2}$. In this molecule. the $K_{a}=1$ component had. by far. the largest asymmetry splining within a given rotational transition and the greatest iniensity. For $\mathrm{MgNH}_{2}$, therefore, strong lines fiting this pattern were preliminarily assigned as $K_{a}=1$. The second $K_{a}$ assignment was made by idenifying another set of strong lines near the centroid of the $K_{a}=1$ components, with smaller asymmetry spliting. These features were assigned to the $K_{d}=3$ components. Once the $K_{a}=1$ and $K_{a}=3$ assignments were made. other asymmetry components were identified by extrapolation to a symmetric top pattem. Tentative $K_{a}$ quantum numbers were assigned. and then asymmetry doublets were collapsed until the $1: 3: 5: 7: 9 \ldots$ pattem found in the $K$ components of a symmetric top was generated.

For $\mathrm{MgND}_{2}, 60 \mathrm{GHz}$ was initially scanned. Since deuterium nuclei are bosons. a $\mathrm{C}_{2}$ rotation in

Fig. I. A section of the $N=18 \rightarrow 19$ spectrum of $\mathrm{MgNH}_{2}\left(\dot{\mathrm{X}}^{2} \mathrm{~A}_{1}\right)$ containing the $\mathbb{K}_{a}=0.2 .3$ and 4 asymmetry components near 496 GHz . Spin-rotation splittings are resolved in every transition. and the effect of nuclear spin statistics is evident in the spectrum. (Odd $K_{0}$ transitions are stronger than even $K_{0}$ ones.) Doublets arising from excited vibrational modes are labeled by an asterisk. This spectrum is a composite of twelve, 100 MHz scans, each lasting 50 s in duration.

$\mathrm{MgND}_{2}$ produces a $2: 1$ intensity ratio for $K_{a}$ even (ortho) vs. $K_{a}$ odd (para) components. Hence, the effect of nuclear spin statistics was not as dramatic as in $\mathrm{MgNH}_{2}$. For the deuterated species, the $K_{a}=3$ and 4 components were assigned first, using their small asymmetry splitings as a basis. as was observed in the spectrum of CaND. Assignment of additional $K_{a}$ components for this molecule was then made in the same way as for $\mathrm{MgNH}_{2}$, namely, collapsing rentatively identified asymmerry doublets until a symmetric top pattem emerged.

Following the initial assignment of the $\mathcal{K}_{a}$ quantum numbers for about three transitions for each molecule. the partial data set was fir io generate preliminary rotational constants. These constants were then used to predict the frequencies for other transitions to an accuracy of $1-2 \mathrm{MHz}$, eliminating the need for extensive frequency searches. In the final data set, 12 rotational transitions of $\mathrm{MgNH}_{2}$ were recorded, iypically for $K_{a}=0$ to 5, with some $K_{a}=7$ measurements. For $\mathrm{MgND}_{2}$, eight transitions were observed for $K_{a}=0$ to 7 . A cotal of 257 and 228 individual lines were measured for $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$, respectively. A representative subset of these data is presented in Table 1. The complete data set can be obtained as supplemental information. ${ }^{2}$

Figure I shows a section of the spectrum of the $N=18 \rightarrow 19$ transition of $\mathrm{MgNH}_{2}$ near 496 GHz , consisting of $K_{d}=0.2 .3$. and 4 components. The spin-rotation spliting for each component is clearly resolved. The asymmetry spliting however, steadily decreases with increasing $K_{a}$ quantum number, such that it is collapsed for the $K_{a}=4$ lines. The effect of the nuclear spin-statistics is also apparent in the specinum. The $K_{a}=3$ features are nearly three times larger than the $K_{a}=2$ lines. for example.

A portion of the $N=20 \rightarrow 21$ transition of $\mathrm{MgND}_{2}$ is presented in Fig. 2, showing $K_{a}=2.3$ and 4 components. In this specirum asymmerry spliting for both the $K_{a}=3$ and 4 lines is readily resolved. This splining is actually greater for the $K_{a}=2$ components. but the higher frequency $K_{a}=2$ line is not included in this spectum. Again. the effect of nuclear spin-stanistics is apparent in the increased

[^2]Fig. 2. Parn of the spectrum of the $N=20 \rightarrow 21$ transition of MgND $\left(\bar{X}^{2} \mathrm{~A}_{1}\right)$ near $473 \mathrm{GH2}$. showing the $K_{a}=3$ and 4 asymmery doublets and one of the $K_{0}=2$ lines. The spin statistics have reversed for the deuterium isoropomer such shat even $K_{n}$ transitions are stronger than odd $\mathbb{K}_{a}$ lines. Spin-fotation interactions are resolved in every iransition. and the doublets marked by an asterisk indicate vibrational satellite features. This specirum was created from a composite of eigh! 100 MHz scans, each with a 50 s scan time.


Fig. 3. A stick figure illustrating the progression of observed $K_{u}$ components in the $N=18 \rightarrow 19$ transition of both $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}\left(\dot{\mathrm{X}}^{2} \mathrm{~A}_{1}\right)$. Spin-rotation splitings have been neglected. The wider spacing of $K_{u}=1$ asymmetry doublets and frequency offiset of the $K_{v}=0$ from the centroid of the $K_{u}=1$ lines indicate that $\mathrm{MgND}_{2}$ is less symmetric than $\mathrm{MgNH}_{2}$. Another manifestation of the larger asymmetry in ine deuterium isotopomer is the presence of the $K_{a}=3,4.5 .6$ and 7 lines at higher frequency relative to the $K_{a}=0$ rransition: in $\mathrm{Mg}_{\mathrm{g}} \mathrm{NH}_{2}$ they lie lower in frequency, as might be expected in the correiation to a symmetric top.

intensity of the even $K_{a}$ lines. Fine siructure splitings are also resolved in every transition.
The substitution of the deutetons for the protons in $\mathrm{MgNH}_{2}$ increases the asymmetry of the molecule. Deuteration shifts the center of mass closer to the $N$ atom. making $M g N D_{2}$ slightly more oblate than its hydrogen analog. The effect of the increased asymmetry on the rotational specirum is seen in Fig.

3, where stick figures of the $N=18 \rightarrow 19$ transitions for both $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ are shown. in the $\mathrm{MgNH}_{2}$ spectrum (top panel), the $K_{a}=1$ components are separated by approximately 9 GHz and only the $K_{a}=1,2$, and 3 have resolvable asymmetry spliting. The $K_{c}=0$ transition is located close to the center of the patterm while most additional $K_{a}$ components are situated lower in frequency relative to this line. For $\mathrm{MgND}_{2}$ (bottom panel), the asymmetry splitting of the $K_{a}=1$ components is approximately 11 GHz . Moreover, the $K_{a}=4$ asymmetry doublets are resolved for $\mathrm{MgND}_{2}$, unlike $\mathrm{MgNH}_{2}$. (This spliting is too small to be seen on the scale of the Fig. 3). The most dramatic change between the spectra of the two isotopomers, however, is the appearance of the $K_{a}=0$ line at a lower frequency relative to the centroid of the $K_{a}=1$ lines for $\mathrm{MgND}_{2}$. Furthermore, the $K_{a}=2,3,4,5,6$, and 7 components now appear at higher frequencies relative to the $K_{a}=0$ transition. This increased asymmetry made the assignment of the $\mathrm{MgND}_{2}$ spectrum more difficult.

## 4. Analysis

The data for $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ were fit io a ${ }^{2} \mathrm{~A}_{1}$ asymmetric sop Hamiltonian of the form

$$
\begin{equation*}
H_{\mathrm{eff}}=H_{\mathrm{rot}}+H_{\mathrm{ed}}+H_{\mathrm{si}} \tag{1}
\end{equation*}
$$

where $H_{\text {roc }}+H_{\text {cd }}$ describe molecular frame rotation and its centrifugal distorion corrections and $H_{s t}$ refers to fine structure interactions. The first two terms in the effective Hamiltonian are [25]

$$
\begin{align*}
& H_{\mathrm{rat}}+H_{\mathrm{cd}}=A N_{x}^{2}+B N_{\underset{Y}{2}+C N_{:}^{2}-D_{N}\left(N^{2}\right)^{2}-D_{N K} N^{2} N_{:}^{2}+d_{1} N^{2}\left(N_{+}^{2}+N_{-}^{2}\right)+d_{2}\left(N_{+}^{4}+N_{-}^{4}\right)} \begin{array}{l}
+H_{N K}\left(N^{2}\right)^{2} N_{:}^{2}+H_{K N} N^{2} N_{:}^{4}+L_{K K N} N^{2} N_{:}^{6}+L_{N N K}\left(N^{2}\right)^{3} N_{z}^{2} \\
\\
\quad+P_{N N K}\left(N^{2}\right)^{3} N_{:}^{4}+P_{K N} N^{2} N_{:}^{8}
\end{array} \text { (2) }
\end{align*}
$$

This Hamithonian is basically the S -reduced form of Watson, with the addition of the higher order centrifugal distonion terms such as $L_{K K N}, L_{N N K}, P_{N N K}$, and $P_{K N}$. The spin-rotation Hamilonian [26] is a tensor with potentially nine terms. For molecules with $\mathrm{C}_{2 v}$ symmerry, however, the off-diagonal elements of this tensor are zero. Hence, the Hamilionian simplifies to include only the diagonal eiements $\epsilon_{a a}, \epsilon_{b}$, and $\epsilon_{c c}$, i.e..
$H_{\mathrm{st}}=\sum_{\sigma} \epsilon_{\alpha \sigma} N_{\alpha} \cdot S_{\alpha}$
where $\alpha$ sums over the three molecule-fixed coordinates. These itree parameters were sufficient to model the spin-rotation splitings for both $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ satisfactorily, and no centrifugal distortion corrections required.

For both molecules, the data were fir using the least-squares fiting program SPFTT [27]. Initially, the lowess $K_{a}$ componenis ( $K_{a}<4$ ) for at least inree rotational iransitions were entered into the program. Only rotational, lower order cenmifugal distorion, and spin-rataion parameters were employed in this initial fit. For $\mathrm{MgNH}_{2}$, the $A$ rotational constant was fixed to a value scaled by mass from those of $\mathrm{CaNH}_{2}$ [18] and $\mathrm{SrNH} \mathrm{S}_{2}$ [19]. Higher $\mathrm{K}_{a}$ components were inen added to the fit, which required higher order cennifugal disfonion parameters to achieve an acceptable mms. Also, at this point, $A$ was no longer constrained. For $\mathrm{MgND}_{2}$, the same fitting procedure was followed, except $A$ was initially fixed to half the value of $A$ of $\mathrm{MgNH}_{2}$.

The final rotational constants determined for ihese two molecules are listed in Table 2 . In both cases, the rms of the final fits is less than 100 kHz , indicating a high degree of precision. It should be noted that $\mathrm{MgND}_{2}$ required two addinional higher order centrifugal distortion constants than $\mathrm{MgNH}_{2}$. The extra terms are expected. since higher energy rotational transitions were observed in $\mathrm{MgND}_{2}$.

Table 2. Spectroscopic constanss of $\mathrm{MgNLD}_{2}$ and MgND:


| Parameter | $\mathrm{MgNH}_{2}$ | $\mathrm{MgND}_{2}$ |
| :---: | :---: | :---: |
| A | 378525(42) | 189900(4) |
| 8 | $13314.7718(47)$ | $11626.5105(57)$ |
| $C$ | 12839.1166 (46) | 10933.0387(51) |
| ${ }_{\text {a }}$ | 24.49(33) | 13.01(36) |
| $6_{6}{ }_{6}$ | 39.743(90) | $34.755(88)$ |
| $\epsilon_{\text {cc }}$ | 37.923(88) | 32.303(80) |
| $D_{n}$ | 0.0215749(28) | $0.0145008(22)$ |
| $D_{N K}$ | $1.86805(29)$ | $1.17624(44)$ |
| $\dot{d}_{1}$ | -0.0008811(37) | -0.0010360(30) |
| $d_{2}$ | -0.0002076(17) | -0.0003729(12) |
| $H_{K N}$ | -0.001184(11) | -0.00027p(37) |
| $H_{H K}$ | $2.886(32) \times 10^{-5}$ | $2.131(36) \times 10^{-5}$ |
| L LMK | - | $-1.55(40) \times 10^{-9}$ |
| $L_{\text {KKA }}$ | - | $-2.1(1.1) \times 10^{-6}$ |
| $P_{\text {R }}$ | $-8.992(30) \times 10^{-7}$ | -3.3 (1.1) $\times 10^{-8}$ |
| $P_{\text {NAK }}$ | $3.60(14) \times 10^{-9}$ | $2.02(50) \times 10^{-11}$ |
| mms | 0.051 | 0.051 |

a In MHz. Errors ane $3 a$ and apply to the last quoted decimal place.

## 5. Discussion

Analysis of both the electronic and rotational spectra of $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$ have demonstrated that these molecules are planar. $\mathrm{MgNH}_{2}$ also appears 80 have this geomerry. Evidence for planarity parly arises from the $3: 1$ intensity variation with $\mathbb{K}_{a}$ quantum number coused by nuclear spin statistics, which changes to a $1: 2$ ratio on deuterium substitution. This variation is apparent in the spectra of $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$, as shown in Figs. 1 and 2, and eliminates the possibility of pyramidal geometry without inversion. A pyramidal structure with inversion can also give rise to the observed intensity pattem for the lower inversion level, but the reverse patern for the upper inversion state musi also be present. Although additional doublets were found in the $\mathrm{MgNH}_{2}$ spectra, for example, as shown in Fig. 1, none of these lines produced the "mirror image" spectrum as required for an upper inversion level. A continuous frequency scan was even conducted between the $N=17 \rightarrow 18$ and $N=18 \rightarrow 19$ transitions but no such state could be idenified. Moreover, the extra lines observed were all quite weak, with intensities no greater than that of the $K_{a}=4$ component of the ground vibrational state of MgNH . These lines are assumed to arise from the low-lying $\nu_{4}$ and $v_{6}$ bending vibrational modes. Both of these states have been identified and analyzed for $\mathrm{CaNH}_{2}$ [18]. Due to the increase in energy above ground state of these levels for $\mathrm{MgNH}_{2}$ compared with $\mathrm{CaNH}_{2}$, however, a sufficient number of $K_{a}$ components could not be observed to assign either vibrational mode.

Additional evidence for planarity arises from the small. positive inerial defect ( $\Delta_{0}$ ) calculazed for $\mathrm{MgNH}_{2}$. For this radical, $\Delta_{0}=0.078$ amu $A^{2}$, which is close to the value for formaldehyde [28], $\Delta_{0}=0.0577$ ame $\AA^{2}$. On deuterium substitution, the inertial defect increases only slightly to $\Delta_{0}=0.096$ and remains positive - another indication of planarity. Some nonplanar molecules such as formamide [29], have positive inerial defects, but they become negative on deuterium substimtion. The inertial defect for $\mathrm{MgNH}_{2}$ also follows the decreasing trend of the other alkaline-earth amides. For $\mathrm{CaNH}_{2}[18], \Delta_{0}=0.157$ and for $\mathrm{SrNH}_{2}[19], \Delta_{0}=0.180$.

Because deuterium substitution has been carried out for $\mathrm{MgNH}_{2}$, an rn structure can be calculated. The results of these calculations are presented in Table 3, along with comparable data for $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$. For calcium and strontium amide, the $\mathrm{N}-\mathrm{H}$ bond length and $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle are almost

Table 3. Geomeries of the alkaline-earh amides."

|  | $\delta_{\mathrm{M}-\mathrm{N}}$ $(A)$ | $\begin{aligned} & { }_{\mathrm{N}-\mathrm{A}} \\ & (A) \end{aligned}$ | $\begin{aligned} & \theta_{B-R-K} \\ & \left.0^{\circ}\right) \end{aligned}$ | Ref. |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{MgNH}_{2}$ | 1.899(3) | $1.007(3)$ | 108.7(5) | This work |
| $\mathrm{CaNH}_{2}$ | $2.126(3)$ | 1.018(3) | 105.8(5) | 18 |
| $\mathrm{SrNH}_{2}$ | $2.256(1)$ | 1.021(1) | 105.4(1) | 19 |

a Enors are based on incrinsic uncertaimbies in the use of substitution strverures. Table 4. Spin-rotation and g-tensor parameters for $\mathrm{MNH}_{2}$ and $\mathrm{MND}_{2}$.

|  | $\mathrm{MgNH}_{2}$ | $\mathrm{CaNH}_{2}{ }^{\text {a }}$ | SrNH ${ }^{6}$ | $\mathrm{MgND}_{2}$ | $\mathrm{CaND}_{2}{ }^{\circ}$ | $\mathrm{SrND}_{2}{ }^{\text {b }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $6_{\text {aco }}{ }^{\circ}$ | 24.49 | 45.7 | 160.4 | 13.01 | 22.4 | 91.3 |
| $\epsilon_{6 s}{ }^{\text {c }}$ | 39.743 | 32.053 | 59.740 | 34.755 | 37.886 | 51.526 |
| $E_{\text {fre }}{ }^{\text {c }}$ | 37.923 | 41.110 | 89.657 | 32.303 | 35.338 | 76.842 |
| gace | 2.0023 | 2.0022 | 2.0021 | 2.0022 | 2.0022 | 2.0021 |
| 885 | 2.00081 | 2.00052 | 1.99790 | 2.00081 | 2.00051 | 1.99787 |
| grom | 2.00082 | 2.00000 | 1.99556 | 2.00082 | 1.99999 | 1.99548 |

${ }^{4}$ Ref. 18.
${ }^{4}$ Ref. 19.
${ }^{r} \ln \mathrm{MHz}$.
identical, with values near $\mathrm{N}-\mathrm{H}=1.02 \AA$ and $\theta_{H-N}-\mathrm{H}=105.6^{\circ}$. However, for $\mathrm{MgNH}_{2}$, the $\mathrm{H}-\mathrm{N}-$ $H$ bond angle increases by nearly $3^{\circ}$ to $108.7^{\circ}$. For ammonia, which has a pyramidal geometry, the projected $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle onto the plane defined by the hydrogen atoms is $120^{\circ}$. (This is a more ditect comparison than the actual $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle of $\mathrm{NH}_{3}$, which is near $107^{\circ}$ ). Hence, the increase in bond angle in $\mathrm{MgNH}_{2}$ may reflect a small increase in covalent character relative io $\mathrm{SrNH}_{2}$ and $\mathrm{CaNH}_{2}$. This increased covalency is not large enough, however, to cause the molecule to become pyramidal in shape. It should be noted that in $\mathrm{NH}_{2}^{-}$, the $\mathrm{H}-\mathrm{N}-\mathrm{H}$ angle is $\approx 103^{\circ}[30]$ - closer to that of $\mathrm{CaNH} \mathrm{H}_{2}$ and $\mathrm{SrNH}_{2}$ than $\mathrm{MgNH}_{2}$.

The electronegativities of $\mathrm{Mg}, \mathrm{Ca}, \mathrm{St}$, and H may give a clue to the changing geometries in the alkaline-earth amides and their relationship io $\mathrm{NH}_{3}$. For Ca and $\mathrm{Sr}_{\text {, the }}$ value of the Pauling electronegativity [31] is 1.0. For magnesium the value is aboun 1.3 , and the electronegativiny for $H$ is near 2.2. The increased electronegativiny of magnesium compared with calcium and stronium likely causes this atom to form bonds with less jonic character that these other two alkaline-earth metals. For hydrogen, the change from ionic to covalent character is even greater. Considering the elecronegativity of beryllium of $1.6, \mathrm{BeNH}_{2}$ may indeed be pyramidal. Another molecule of interest is $\mathrm{AlNH}_{2}$. Aluminum has an electronegativity of 1.6 , and might be pyramidal as well.

Another interesting difference between magnesium amide and $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$ arises from the spin-rotation constants, listed in Table 4. As the table shows, $\epsilon_{a g}$ is the lagest spin-rotation tem for $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$, and the smallest is $\epsilon_{b b}$. The opposite is true for $\mathrm{MgNH}_{2}$, where $\epsilon_{b b}$ is the largest and $\epsilon_{a a}$ the smallest of these three parameters. A similar trend is found in the three deuterated species. These differences result in the spin-rotation spliting decreasing with $K_{a}$ quantum number for $\mathrm{CaNH}_{2}$ and $\mathrm{Sr} \mathrm{NH}_{2}$, but increasing for $\mathrm{MgNH}_{2}$.

Some of these variations, of course, are because of changes in mass. The mass-dependent effects can be minimized by calculating the $g$-tensor for each molecule, which gives a better insight into electronic propenies of these species. As shown by Curl [32] and Dixon [33], the spin-rotation parameters are related to the eleciron $g$-tensor, $g_{a \alpha}$, by the following equation:
$g_{a \alpha}=2.0023-\frac{\epsilon_{\alpha a}}{2 B_{\alpha}}$

Fig. 4. An idealized structure of $\mathrm{MgNH} H_{2}$ showing the relationship berween the molecule fixed $\hat{\hat{a}} . \hat{\mathrm{b}}$, and $\hat{\varepsilon}$ axes, the space-fixed axes, and the orientation of the $p_{x}\left(t_{1}\right)$ and $p_{y}\left(b_{2}\right)$ ortitals on the magnesium atom. The $\hat{a}$ and $\hat{b}$ axes define the plane of the molecule, which also contains the $\mathrm{p}_{y}\left(\mathrm{~b}_{2}\right)$ orbital. The $\hat{\mathrm{c}}$ axis lies perpendicular io this plane, as does the $p_{r}\left(\mathrm{~b}_{1}\right)$ orbital.

where $\epsilon_{\text {ra }}$ is the spin-rotation constant for the a molecule-fixed axis and $B_{q}$ is the corresponcling rotational constant. The $g$-factor for the free electron is 2.0023 . From this expression, the $g$-tensor for all three alkaline-eant amide species has been calculated and the values are presented in Table 4. They have been additionally calculated for the deuterium isotopomers for an accuracy comparison. As the table shows, the main isotope and the deuterated forms have identical $g$-tensor elements to the fourth decimal place.

The unpaired electron of these metal amide species in their electronic ground state resides in a predominantly $a_{1}$ orbital, which is of course spherically symmetric and arises from an atomic orbital on the metal atom. The $g$-tensor elements, therefore, should, to a first approximation, reflect the isotropy of this electron and have quantities very near the free electron value of 2.0023 . Indeed, gaa for all species listed in Table 4 is very close to this number. For $g_{b b}$ and $g_{c c}$, the situation changes. In $\mathrm{SrNH}_{2}$ and $\mathrm{CaNH}_{2}, 8_{r s}$ deviates noticeably from the free electron value ( 1.99556 and 2.00000 ), and 806 has a value in between that of $g_{a a}$ and $g e c$ ( 1.99790 and 2.00052 ). Therefore. the tensor elements differ most from the free electron value in the $\hat{c}$-direction (or $\bar{x}$-direction) for $\mathrm{CaNH}_{2}$ and SrNH , indicating the most anisotropy along this axis, which is perpendicular to the plane of the molecule (see Fig. 4). This change may be due to mixing of the unoccupied atomic $p_{x}$ orbital into the molecular orbital of the metal. There is also a smaller contribution from the py atomic orbital as well. These orbitals are the primary coniributors to the molecular orbitals of the unpaired electron in the excited $\mathrm{B}_{1}$ and $\mathrm{B}_{2}$ states. As noted by Dixon [33], departure from free-spin values in the $g$-iensor can be anributed to the spin-orbit contribution to the spin-fotation interaction. The $\mathbb{B}_{1}$ and $\mathrm{B}_{2}$ states may be perurbing the ground state through this type of interaction. (Strictly speaking, there is no spin-orbir coupling in $B_{1}$ and $\mathrm{B}_{2}$ states, bur the effecis remain, for example, in the very large $\epsilon_{a n}$ constants in these states which result from mixing of the $\mathrm{p}_{x}$ and $\mathrm{p}_{y}$ orbitals in $\mathrm{CaNH} \mathrm{C}_{2}$ and $\mathrm{S}_{5} \mathrm{NH}_{2}$. These two states correlate back to the spin-orbit components of a ${ }^{2} \overline{7}$ state in the linear limit [34].)

For $\mathrm{MgNH}_{2}$, the $g$-tensor is different from that of $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$. In this case the largest deviation from the free electron value is $g b b$, which is 2.00081 , while $g_{c c}$ is 2.00082 . Although these

Fig. 5. An idealized figure showing the orientations of the predominant p-iype orbital contributing to the unpaired electron distribution in $\mathrm{MNH}_{2}$ species. These figures are based on the $g$-tensor calculations. For $\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$. the out-of-plane orbital appears to contribure the most to the anisorropy. For $\mathrm{MgNH}_{2}$, the in-plane one is slightly more imponant. and may indicate an evenual evolution to the pyramidal geometry, the probable structure for $\mathrm{BeNH}_{2}$.

$\mathrm{CaNH}_{2}, \mathrm{SrNH}_{2}$ (planar)

(planar)

$\mathrm{BeNH}_{2}$ ?
(pyramidal)
differences are small. they are duplicated in the $\mathrm{MgND}_{2} g$-tensor, and hence are likely real effects. In $\mathrm{MgNH}_{2}$. the greatest anisotropy is thus in the $\hat{b}$-direction, in the molecular plane, which likely arises from mixing of the $p_{y}$ atomic orbital of magnesium into the molecular orbital of the unpaired electron. Consequently, there appears to be a small shift in the anisotropic electron distribution in $\mathrm{MgNH}_{2}$ relative $10 \mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$. In calcium and strontium amide. there is slightly more our-of-plane p-iype orbital character for the unpaired electron in the $\bar{X}^{2} A_{1}$ state. but more in-plane $p$-type character for the unpaired electron in $\mathrm{MgNH}_{2}$. A schematic showing this change is presented in Fig. 5.

The out-of plane orbital characier in $\mathrm{CaNH}_{2}$ and $\mathrm{SiNH}_{2}$ perhaps arises because the unpaired electron is avoiding the electron densities of the $M-N$ bond and the $\mathrm{N}-\mathrm{H}$ bonds, which all lie in the molecular plane. The slight redistribution of she electron density inio the in-plane orbital in $\mathrm{MgNH}_{2}$ may be a resuln of a subtle increase in covalent character of this species and the correlation to the predominately covalent pyramidal geometry. For pyramidal $\mathrm{MNH}_{2}$, the preferred orientation of any p-orbital of the unpaired electron would likely be perpendicular to the pseudo $\mathrm{C}_{3}$ axis defined by the nitrogen atom (see Fig. 5). This arrangement avoids other electron distributions, as in the $\mathrm{M}-\mathrm{N}$ bond. 1 t is this orientation that would appear to correlate with the in-plane $p_{y}$ orbital in the $C_{2 v}$ system.

## 6. Conclusion

Measurement of the pure rotational spectra of $\mathrm{MgNH}_{2}$ and $\mathrm{MgND}_{2}$ - the first study of magnesium amide to date - has shown that this alkaline-earth amide is planar in its $\bar{X}^{2} A_{1}$ ground electronic state. Hence, this molecule follows the structural pattem of $\mathrm{CaNH} \mathrm{H}_{2}$ and $\mathrm{SrNH}_{2}$. However. there are some subtle differences between $\mathrm{MgNH}_{2}$ and its strontium and calcium analogs. For example. comparison of $r_{0}$ structures show that the $\mathrm{H}-\mathrm{N}-\mathrm{H}$ bond angle is $3^{\circ}$ larger in $\mathrm{MgNH}_{2}$ than in $\mathrm{CaNH} \mathrm{N}_{2}$ and $\mathrm{SiNH}_{2}$, both which have comparable angles. Also, the orbital character of the unpaired electron in $\mathrm{MgNH}_{2}$ appears to slighty favor the coniribution of the in-plane $p_{y}$ orbital. as opposed to the our-of-plane $p_{x}$ orbital for
$\mathrm{CaNH}_{2}$ and $\mathrm{SrNH}_{2}$. These variations likely indicate a small increase in covalent character in $\mathrm{MgNH}_{2}$, as might be expected considering electronegativity differences of the alkaline-eath meals. Spectroscopic studies of the excited electronic states of magnesium amide, as well as BeNH 2 and AlNH 2 , would provide additional insight into metal-ligand interactions in amide species.

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Supplemental Table 1
OBSERVED TRANSITION FREQUENCIES OF $\operatorname{MgNH} H_{2}$ AND MgND ${ }_{2}\left(\bar{X}^{2} \mathrm{~A}_{1}\right)^{a)}$

| N | $\mathrm{K}^{\text {a }}$ | $\mathrm{K}^{\prime}{ }^{\prime}$ | J | N* | $\mathrm{K}^{\prime \prime}$ | $\mathrm{K}_{*}{ }^{\prime \prime}$ | $J^{\prime \prime}$ | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $V_{\text {obs }}$ | $v_{0-c}$ | $V_{\text {cobs }}$ | $v_{0-5}$ |
| 5 | 1 | 5 | 4.5 | 4 | 1 | 4 | 3.5 | 129529.697 | -0.008 |  |  |
| 5 | 1 | 5 | 5.5 | 4 | 1 | 4 | 4.5 | 129568.688 | 0.010 |  |  |
| 5 | 1 | 4 | 4.5 | 4 | 1 | 3 | 3.5 | 131906.673 | 0.034 |  |  |
| 5 | 1 | 4 | 5.5 | 4 | 1 | 3 | 4.5 | 131946.543 | 0.021 |  |  |
| 6 | 1 | 6 | 5.5 | 5 | 1 | 5 | 4.5 | 155432.918 | -0.030 |  |  |
| 6 | 1 | 6 | 6.5 | 5 | 1 | 5 | 5.5 | 155471.705 | -0.027 |  |  |
| 6 | 1 | 5 | 5.5 | 5 | 1 | 4 | 4.5 | 158284.859 | -0.028 |  |  |
| 6 | 1 | 5 | 6.5 | 5 | 1 | 4 | 5.5 | h58324.558 | -0.023 |  |  |
| 9 | 1 | 9 | 8.5 | 8 | 1 | 8 | 7.5 | 233117.964 | -0.062 |  |  |
| 9 | 1 | 9 | 9.5 | 8 | 1 | 8 | 8.5 | 233156.535 | -0.039 | $i$. |  |
| 9 | 3 | 7 | 8.5 | 8 | 3 | 6 | 7.5 | 235005.777 | 0.021 |  |  |
| 9 | 3 | 6 | 8.5 | 8 | 3 | 5 | 7.5 | 235005.777 | -0.098 |  |  |
| 9 | 3 | 7 | 9.5 | 8 | 3 | 6 | 8.5 | 235046.269 | 0.061 |  |  |
| 9 | 3 | 6 | 9.5 | 8 | 3 | 5 | 8.5 | 235046.269 | -0.058 |  |  |
| 9 | 2 | 8 | 9.5 | 8 | 2 | 7 | 8.5 | 235199.672 | 0.114 |  |  |
| 9 | 2 | 7 | 8.5 | 8 | 2 | 6 | 7.5 | 235214.423 | -0.020 |  |  |
| 9 | 0 | 9 | 8.5 | 8 | 0 | 8 | 7.5 | 235247.037 | -0.003 |  |  |
| 9 | 2 | 7 | 9.5 | 8 | 2 | 6 | 8.5 | 235254.050 | 0.026 |  |  |
| 9 | 0 | 9 | 9.5 | 8 | 0 | 8 | 8.5 | 235285.788 | -0.049 |  |  |
| 9 | 1 | 8 | 8.5 | 8 | 1 | 7 | 7.5 | 237393.209 | 0.000 |  |  |
| 9 | 1 | 8 | 9.5 | 8 | 1 | 7 | 8.5 | 237432.665 | -0.003 |  |  |
| 10 | 1 | 10 | 9.5 | 9 | 1 | 9 | 8.5 | 259002.845 | -0.012 |  |  |
| 10 | 1 | 10 | 10.5 | 9 | 1 | 9 | 9.5 | 259041.445 | 0.076 |  |  |
| 10 | 5 | 6 | 9.5 | 9 | 5 | 5 | 8.5 | 260482.444 | 0.012 |  |  |
| 10 | 5 | 5 | 9.5 | 9 | 5 | 4 | 8.5 | 260482.444 | 0.012 |  |  |
| 10 | 5 | 6 | 10.5 | 9 | 5 | 5 | 9.5 | 260524.961 | 0.071 |  |  |
| 10 | 5 | 5 | 10.5 | 9 | 5 | 4 | 9.5 | 260524.961 | 0.071 |  |  |
| 10 | 4 | 7 | 9.5 | 9 | 4 | 6 | 8.5 | 260834.586 | -0.120 |  |  |
| 10 | 4 | 6 | 9.5 | 9 | 4 | 5 | 8.5 | 260834.586 | -0.120 |  |  |
| 10 | 4 | 7 | 10.5 | 9 | 4 | 6 | 9.5 | 260875.763 | -0.098 |  |  |
| 10 | 4 | 6 | 10.5 | 9 | 4 | 5 | 9.5 | 260875.763 | -0.098 |  |  |
| 10 | 3 | 8 | 9.5 | 9 | 3 | 7 | 8.5 | 261105.610 | 0.068 |  |  |
| 10 | 3 | 7 | 9.5 | 9 | 3 | 6 | 8.5 | 261105.610 | -0.136 |  |  |
| 10 | 3 | 8 | 10.5 | 9 | 3 | 7 | 9.5 | 261145.824 | 0.139 |  |  |
| 10 | 3 | 7 | 10.5 | 9 | 3 | 6 | 9.5 | 261145.824 | -0.066 |  |  |
| 10 | 2 | 9 | 9.5 | 9 | 2 | 8 | 8.5 | 261272.533 | -0.056 |  |  |
| 10 | 2 | 9 | 10.5 | 9 | 2 | 8 | 9.5 | 261312.022 | 0.027 |  |  |
| 10 | 2 | 8 | 9.5 | 9 | 2 | 7 | 8.5 | 261347.326 | -0.081 |  |  |
| 10 | 0 | 10 | 9.5 | 9 | 0 | 9 | 8.5 | 261356.691 | -0.015 |  |  |
| 10 | 2 | 8 | 10.5 | 9 | 2 | 7 | 9.5 | 261386.849 | -0.008 |  |  |

Supplemental Table 1 cont.

| N | $\mathrm{K}^{\prime}{ }^{\prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | $J$ | $\mathrm{N}^{\prime \prime}$ | K ${ }^{\circ \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | J" | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {obs }}$ | $v_{\infty}$ | $v_{\text {ots }}$ | $V_{\text {boc }}$ |
| 10 | 0 | 10 | 10.5 | 9 | 0 | 9 | 9.5 | 261395.576 | 0.081 |  |  |
| 10 |  | 9 | 9.5 | 9 | 1 | 8 | 8.5 | 263751.622 | -0.077 |  |  |
| 10 | 1 | 9 | 10.5 | 9 | 1 | 8 | 9.5 | 263791.167 | 0.046 |  |  |
| 12 | 1 | 12 | 11.5 | 11 | 1 | 11 | 10.5 | 310753.521 | -0.099 | 266278.391 | -0.036 |
| 12 | 1 | 12 | 12.5 | 11 | 1 | 11 | 11.5 | 310792.130 | 0.048 | 266311.383 | -0.043 |
| 12 | 7 | 6 | 11.5 | 11 | 7 | 5 | 10.5 | 311302.332 | -0.093 |  |  |
| 12 | 7 | 5 | 11.5 | 11 | 7 | 4 | 10.5 | 311302.332 | -0.093 |  |  |
| 12 | 7 | 6 | 12.5 | 11 | 7 | 5 | 11.5 | 311346.159 | -0.017 |  |  |
| 12 | 7 | 5 | 12.5 | 11 | 7 | 4 | 11.5 | 311346.159 | -0.017 |  |  |
| 12 | 6 | 7 | 11.5 | 11 | 6 | 6 | 10.5 |  |  | 269592.040 | 0.011 |
| 12 | 6 | 6 | 11.5 | 11 | 6 | 5 | 10.5 |  |  | 269592.040 | 0.011 |
| 12 | 6 | 7 | 12.5 | 11 | 6 | 6 | 11.5 |  |  | 269630.747 | 0.014 |
| 12 | 6 | 6 | 12.5 | 11 | 6 | 5 | 11.5 |  |  | 269630.747 | 0.014 |
| 12 | 5 | 8 | 11.5 | 11 | 5 | 7 | 10.5 | 312541.621 | 0.015 | 269916.528 | 0.036 |
| 12 | 5 | 7 | 11.5 | 11 | 5 | 6 | 10.5 | 312541.621 | 0.015 | 269916.528 | 0.036 |
| 12 | 5 | 8 | 12.5 | 11 | 5 | 7 | 11.5 | 312582.988 | 0.038 | 269953.635 | 0.013 |
| 12 | 5 | 7 | 12.5 | 11 | 5 | 6 | 11.5 | 312582.988 | 0.038 | 269953.635 | 0.013 |
| 12 | 4 | 9 | 11.5 | 11 | 4 | 8 | 10.5 | 312964.246 | -0.098 | 270187.749 | -0.013 |
| 12 | 4 | 8 | 11.5 | 11 | 4 | 7 | 10.5 | 312964.246 | -0.099 | 270187.749 | -0.046 |
| 12 | 4 | 9 | 12.5 | 11 | 4 | 8 | 11.5 | 313004.712 | $-0.076$ | 270223.660 | 0.054 |
| 12 | 4 | 8 | 12.5 | 11 | 4 | 7 | 11.5 | 313004.712 | -0.076 | 270223.660 | 0.021 |
| 12 | 3 | 10 | 11.5 | 11 | 3 | 9 | 10.5 | 313291.099 | 0.253 | 270416.631 | -0.027 |
| 12 | 3 | 9 | 11.5 | 11 | 3 | 8 | 10.5 | 313291.099 | -0.264 | 270423.647 | -0.093 |
| 12 | 3 | 10 | 12.5 | 11 | 3 | 9 | 11.5 | 313330.869 | 0.279 | 270451.492 | -0.018 |
| 12 | 3 | 9 | 12.5 | 11 | 3 | 8 | 11.5 | 313330.869 | -0.238 | 270458.652 | 0.055 |
| 12 | 2 | 11 | 11.5 | 11 | 2 | 10 | 10.5 | 313479.463 | -0.023 | 270396.677 | 0.009 |
| 12 | 2 | 11 | 12.5 | 11 | 2 | 10 | 11.5 | 313518.722 | 0.011 | 270430.814 | 0.085 |
| 12 | 0 | 12 | 11.5 | 11 | 0 | 11 | 10.5 | 313545.675 | -0.021 | 270023.288 | -0.050 |
| 12 | 0 | 12 | 12.5 | 11 | 0 | 11 | 11.5 | 313584.492 | 0.027 | 270056.628 | 0.018 |
| 12 | 2 | 10 | 11.5 | 11 | 2 | 9 | 10.5 | 313608.988 | -0.070 | 270965.703 | -0.070 |
| 12 | 2 | 10 | 12.5 | 11 | 2 | 9 | 11.5 | 313648.368 | 0.021 | 271000.047 | -0.045 |
| 12 | 1 | 11 | 11.5 | 11 | 1 | 10 | 10.5 | 316448.287 | -0.042 | 274577.947 | -0.125 |
| 12 | , | 11 | 12.5 | 11 | 1 | 10 | 11.5 | 316487.734 | 0.033 | 274612.356 | 0.065 |
| 13 | 1 | 13 | 12.5 | 12 |  | 12 | 11.5 | 336618.274 | -0.077 |  |  |
| 13 | 1 | 13 | 13.5 | 12 | 1 | 12 | 12.5 | 336656.836 | 0.040 |  |  |
| 13 | 7 | 7 | 12.5 | 12 | 7 | 6 | 11.5 | 337221.352 | -0.053 |  |  |
| 13 | 7 | 6 | 12.5 | 12 | 7 | 5 | 11.5 | 337221.352 | -0.053 |  |  |
| 13 | 7 | 7 | 13.5 | 12 | 7 | 6 | 12.5 | 337264.433 | 0.008 |  |  |
| 13 | 7 | 6 | 13.5 | 12 | 7 | 5 | 12.5 | 337264.433 | 0.008 |  |  |
| 13 | 5 | 9 | 12.5 | 12 | 5 | 8 | 11.5 | 338562.719 | 0.033 |  |  |
| 13 | 5 | 8 | 12.5 | 12 | 5 | 7 | 11.5 | 338562.719 | 0.033 |  |  |
| 13 | 5 | 9 | 13.5 | 12 | 5 | 8 | 12.5 | 338603.712 | 0.054 |  |  |
| 13 | 5 | 8 | 13.5 | 12 | 5 | 7 | 12.5 | 338603.712 | 0.054 |  |  |
| 13 | 4 | 10 | 12.5 | 12 | 4 | 9 | 11.5 | 339020.704 | $-0.067$ |  |  |


| $\mathrm{N}^{*}$ | K ${ }^{\prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text { }}$ | J | $\mathrm{N}^{*}$ | $\mathrm{K}_{3}{ }^{*}$ | $\mathbb{K}_{\text {c }}{ }^{\prime \prime}$ | $\mathrm{J}^{\text {m }}$ | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $\nu_{\text {obs }}$ | $v_{\text {occ }}$ | $v_{\text {bbs }}$ | $v_{\text {oc }}$ |
| 13 | 4 | 9 | 12.5 | 12 | 4 | 8 | 11.5 | 339020.704 | -0.068 |  |  |
| 13 | 4 | 10 | 13.5 | 12 | 4 | 9 | 12.5 | 339060.950 | -0.026 |  |  |
| 13 | 4 | 9 | 13.5 | 12 | 4 | 8 | 12.5 | 339060.950 | -0.027 |  |  |
| 13 | 3 | 11 | 12.5 | 12 | 3 | 10 | 11.5 | 339375.494 | 0.028 |  |  |
| 13 | 3 | 10 | 12.5 | 12 | 3 | 9 | 11.5 | 339376.098 | -0.143 |  |  |
| 13 | 3 | 11 | 13.5 | 12 | 3 | 10 | 12.5 | 339415.171 | 0.094 |  |  |
| 13 | 3 | 10 | 13.5 | 12 | 3 | 9 | 12.5 | 339415.794 | -0.058 |  |  |
| 13 | 2 | 12 | 12.5 | 12 | 2 | 11 | 11.5 | 339572.649 | 0.002 |  |  |
| 13 | 2 | 12 | 13.5 | 12 | 2 | 11 | 12.5 | 339611.841 | 0.032 |  |  |
| 13 | 0 | 13 | 12.5 | 12 | 0 | 12 | 11.5 | \|339623.100 | 0.017 |  |  |
| 13 | 0 | 13 | 13.5 | 12 | 0 | 12 | 12.5 | 1339661.899 | 0.058 |  |  |
| 13 | 2 | 11 | 12.5 | 12 | 2 | 10 | 11.5 | 339737.470 | 0.002 | , |  |
| 13 | 2 | 11 | 13.5 | 12 | 2 | 10 | 12.5 | 339776.741 | 0.036 |  |  |
| 13 | 1 | 12 | 12.5 | 12 | 1 | 11 | 11.5 | 342785.091 | -0.060 |  |  |
| 13 | 1 | 12 | 13.5 | 12 | 1 | 11 | 12.5 | 342824.527 | 0.021 |  |  |
| 14 | , | 14 | 13.5 | 13 | 1 | 13 | 12.5 | 362475.169 | -0.013 |  |  |
| 14 | 1 | 14 | 14.5 | 13 | 1 | 13 | 13.5 | 362513.656 | 0.043 |  |  |
| 14 | 7 | 8 | 13.5 | 13 | 7 | 7 | 12.5 | 363134.319 | 0.056 |  |  |
| 14 | 7 | 7 | 13.5 | 13 | 7 | 6 | 12.5 | 363134.319 | 0.056 |  |  |
| 14 | 7 | 8 | 14.5 | 13 | 7 | 7 | 13.5 | 363176.718 | 0.014 |  |  |
| 14 | 7 | 7 | 14.5 | 13 | 7 | 6 | 13.5 | 363176.718 | 0.014 |  |  |
| 14 | 5 | 10 | 13.5 | 13 | 5 | 9 | 12.5 | 364577.499 | 0.017 |  |  |
| 14 | 5 | 9 | 13.5 | 13 | 5 | 8 | 12.5 | 364577.499 | 0.017 |  |  |
| 14 | 5 | 10 | 14.5 | 13 | 5 | 9 | 13.5 | 364618.148 | -0.010 |  |  |
| 14 | 5 | 9 | 14.5 | 13 | 5 | 8 | 13.5 | 364618.148 | -0.010 |  |  |
| 14 | 4 | 11 | 13.5 | 13 | 4 | 10 | 12.5 | 365070.881 | -0.104 |  |  |
| 14 | 4 | 10 | 13.5 | 13 | 4 | 9 | 12.5 | 365070.881 | -0.106 |  |  |
| 14 | 4 | 11 | 14.5 | 13 | 4 | 10 | 13.5 | 365110.944 | -0.057 |  |  |
| 14 | 4 | 10 | 14.5 | 13 | 4 | 9 | 13.5 | 365110.944 | -0.059 |  |  |
| 14 | 3 | 12 | 13.5 | 13 | 3 | 11 | 12.5 | 365454.187 | 0.066 |  |  |
| 14 | 3 | 11 | 13.5 | 13 | 3 | 10 | 12.5 | 365455.387 | 0.140 |  |  |
| 14 | 3 | 12 | 14.5 | 13 | 3 | 11 | 13.5 | 365493.642 | 0.015 |  |  |
| 14 | 3 | 11 | 14.5 | 13 | 3 | 10 | 13.5 | 365494.789 | 0.034 |  |  |
| 14 | 2 | 13 | 13.5 | 13 | 2 | 12 | 12.5 | 365658.156 | $-0.016$ |  |  |
| 14 | 0 | 14 | 13.5 | 13 | 0 | 13 | 12.5 | 365687.742 | -0.038 |  |  |
| 14 | 2 | 13 | 14.5 | 13 | 2 | 12 | 13.5 | 365697.346 | 0.061 |  |  |
| 14 | 0 | 14 | 14.5 | 13 | 0 | 13 | 13.5 | 365726.581 | 0.055 |  |  |
| 14 | 2 | 12 | 13.5 | 13 | 2 | 11 | 12.5 | 365864.039 | -0.032 |  |  |
| 14 | 2 | 12 | 14.5 | 13 | 2 | 11 | 13.5 | 365903.280 | 0.009 |  |  |
| 14 | 1 | 13 | 13.5 | 13 | , | 12 | 12.5 | 369113.383 | -0.047 |  |  |
| 14 | 1 | 13 | 14.5 | 13 | 1 | 12 | 13.5 | 369152.807 | 0.037 |  |  |
| 15 | 1 | 15 | 14.5 | 14 | 1 | 14 | 13.5 | 388323.508 | -0.010 | 332691.336 | -0.021 |
| 15 |  | 15 | 15.5 | 14 |  | 14 | 14.5 | 388361.975 | 0.039 | 332724.277 | 0.006 |
| 15 | 7 | 9 | 14.5 | 14 | 7 | 8 | 13.5 | 389040.554 | -0.005 | 336458.53] | -0.066 |

Supplemental Table 1 cont.

| $\mathrm{N}^{\prime}$ | $\mathrm{K}_{\mathrm{a}}{ }^{\prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\text {' }}$ | J | ${ }^{\prime \prime}$ | 发" | $\mathrm{K}_{8}{ }^{\prime \prime}$ | ${ }^{\text {J }}$ | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {obs }}$ | $v_{\text {occ }}$ | $\nu^{\text {coss }}$ | $v_{\text {os }}$ |
| 15 | 7 | 8 | 14.5 | 14 | 7 | 7 | 13.5 | 389040.554 | -0.005 | 336458.531 | -0.066 |
| 15 | 7 | 9 | 15.5 | 14 | 7 | 8 | 14.5 | 389082.570 | 0.037 | 336496.631 | 0.006 |
| 15 | 7 | 8 | 15.5 | 14 | 7 | 7 | 14.5 | 389082.570 | 0.037 | 336496.631 | 0.006 |
| 15 | 6 | 10 | 14.5 | 14 | 6 | 9 | 13.5 |  |  | 336940.770 | -0.011 |
| 15 | 6 | 9 | 14.5 | 14 | 6 | 8 | 13.5 |  |  | 336940.770 | -0.011 |
| 15 | 6 | 10 | 15.5 | 14 | 6 | 9 | 14.5 |  |  | 336977.648 | 0.027 |
| 15 | 6 | 9 | 15.5 | 14 | 6 | 8 | 14.5 |  |  | 336977.648 | 0.027 |
| 15 | 5 | 11 | 14.5 | 14 | 5 | 10 | 13.5 | 390585.583 | 0.058 | 337350.028 | -0.011 |
| 15 | 5 | 10 | 14.5 | 14 | 5 | 9 | 13.5 | 390585.583 | 0.058 | 337350.028 | -0.011 |
| 15 | 5 | 11 | 15.5 | 14 | 5 | 10 | 14.5 | 390625.993 | 0.029 | 337385.898 | 0.021 |
| 15 | 5 | 10 | 15.5 | 14 | 5 | 9 | 14.5 | 390625.993 | 0.029 | 337385.898 | 0.021 |
| 15 | 4 | 12 | 14.5 | 14 | 4 | 11 | 13.5 | 391114.484 | -0.033 | 337697.964 | 0.049 |
| 15 | 4 | 11 | 14.5 | 14 | 4 | 10 | 13.5 | 391114.484 | -0.037 | 337697.964 | -0.112 |
| 15 | 4 | 12 | 15.5 | 14 | 4 | 11 | 14.5 | 391154.343 | -0.039 | 337733.033 | 0.094 |
| 15 | 4 | 11 | 15.5 | 14 | 4 | 10 | 14.5 | 391154.343 | -0.043 | 337733.033 | -0.067 |
| 15 | 3 | 13 | 14.5 | 14 | 3 | 12 | 13.5 | 391526.348 | -0.002 | 338000.367 | -0.042 |
| 15 | 3 | 12 | 14.5 | 14 | 3 | 11 | 13.5 | 391527.982 | 0.036 | 338022.294 | 0.026 |
| 15 | 3 | 13 | 15.5 | 14 | 3 | 12 | 14.5 | 391565.804 | 0.032 | 338034.818 | 0.010 |
| 15 | 3 | 12 | 15.5 | 14 | 3 | 11 | 14.5 | 391567.405 | 0.036 | 338056.652 | -0.029 |
| 15 | 2 | 14 | 14.5 | 14 | 2 | 13 | 13.5 | 391735.441 | -0.037 | 337864.069 | 0.008 |
| 15 | 0 | 15 | 14.5 | 14 | 0 | 14 | 13.5 | 391738.824 | -0.006 | 337063.703 | -0.035 |
| 15 | 2 | 14 | 15.5 | 14 | 2 | 13 | 14.5 | 391774.575 | 0.024 | 337897.946 | 0.055 |
| 15 | 0 | 15 | 15.5 | 14 | 0 | 14 | 14.5 | 391777.601 | 0.038 | 337096.893 | 0.023 |
| 15 | 2 | 13 | 14.5 | 14 | 2 | 12 | 13.5 | 391988.697 | -0.016 | 338970.775 | -0.076 |
| 15 | 2 | 13 | 15.5 | 14 | 2 | 12 | 14.5 | 392027.889 | 0.003 | 339005.051 | -0.026 |
| 15 | 1 | 14 | 14.5 | 14 | 1 | 13 | 13.5 | 395432.510 | 0.006 | 343042.988 | -0.001 |
| 15 | 1 | 14 | 15.5 | 14 | 1 | 13 | 14.5 | 395471.847 | 0.016 | 343077.161 | 0.046 |
| 16 | 1 | 16 | 15.5 | 15 | 1 | 15 | 14.5 |  |  | 354807.043 | -0.007 |
| 16 | 1 | 16 | 16.5 | 15 | 1 | 15 | 15.5 |  |  | 354839.912 | -0.028 |
| 16 | 7 | 10 | 15.5 | 15 | 7 | 9 | 14.5 |  |  | 358867.475 | 0.006 |
| 16 | 7 | 9 | 15.5 | 15 | 7 | 8 | 14.5 |  |  | 358867.475 | 0.006 |
| 16 | 7 | 10 | 16.5 | 15 | 7 | 9 | 15.5 |  |  | 358904.954 | 0.001 |
| 16 | 7 | 9 | 16.5 | 15 | 7 | 8 | 15.5 |  |  | 358904.954 | 0.001 |
| 16 | 0 | 16 | 15.5 | 15 | 0 | 15 | 14.5 |  |  | 359346.456 | -0.020 |
| 16 | 0 | 16 | 16.5 | 15 | 0 | 15 | 15.5 |  |  | 359379.574 | 0.018 |
| 16 | 6 | 11 | 15.5 | 15 | 6 | 10 | 14.5 |  |  | 359382.400 | -0.012 |
| 16 | 6 | 10 | 15.5 | 15 | 6 | 9 | 14.5 |  |  | 359382.400 | -0.012 |
| 16 | 6 | 11 | 16.5 | 15 | 6 | 10 | 15.5 |  |  | 359418.855 | 0.002 |
| 16 | 6 | 10 | 16.5 | 15 | 6 | 9 | 15.5 |  |  | 359418.855 | 0.002 |
| 16 | 5 | 12 | 15.5 | 15 | 5 | 11 | 14.5 |  |  | 359820.573 | 0.005 |
| 16 | 5 | 11 | 15.5 | 15 | 5 | 10 | 14.5 |  |  | 359820.573 | 0.004 |
| 16 | 5 | 12 | 16.5 | 15 | 5 | 11 | 15.5 |  |  | 359856.174 | 0.044 |
| 16 | 5 | 11 | 16.5 | 15 | 5 | 10 | 15.5 |  |  | 359856.174 | 0.043 |
| 16 | 4 | 13 | 15.5 | 15 | 4 | 12 | 14.5 |  |  | 360195.398 | 0.096 |

Supplemental Table 1 cont.

| N | $\mathrm{K}^{\text {s }}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | J | $\mathrm{N}^{\prime \prime}$ | $\mathrm{K}^{*}{ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $J^{\prime \prime}$ | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {obs }}$ | $v_{\text {ors }}$ | $v_{\text {obs }}$ | $v_{\text {osc }}$ |
| 16 | 4 | 12 | 15.5 | 15 | 4 | 11 | 14.5 |  |  | 360195.398 | -0.158 |
| 16 | 4 | 13 | 16.5 | 15 | 4 | 12 | 15.5 |  |  | 360230.299 | 0.148 |
| 16 | 4 | 12 | 16.5 | 15 | 4 | 11 | 15.5 |  |  | 360230.299 | -0.106 |
| 16 | 2 | 15 | 15.5 | 15 | 2 | 14 | 14.5 |  |  | 360334.025 | 0.084 |
| 16 | 2 | 15 | 16.5 | 15 | 2 | 14 | 15.5 |  |  | 360367.796 | 0.078 |
| 16 | 3 | 14 | 15.5 | 15 | 3 | 13 | 14.5 |  |  | 360523.862 | -0.079 |
| 16 | 3 | 13 | 15.5 | 15 | 3 | 12 | 14.5 |  |  | 360554.176 | -0.011 |
| 16 |  | 14 | 16.5 | 15 | 3 | 13 | 15.5 |  |  | 360558.337 | 0.092 |
| 16 | 3 | 13 | 16.5 | 15 | 3 | 12 | 15.5 | 1 |  | 360588.549 | 0.040 |
| 16 | 2 | 14 | 15.5 | 15 | 2 | 13 | 14.5 | 1 |  | 361673.406 | $-0.073$ |
| 16 | 2 | 14 | 16.5 | 15 | 2 | 13 | 15.5 | 1 |  | 361707.665 | -0.038 |
| 16 | , | 15 | 15.5 | 15 | 1 | 14 | 14.5 |  |  | 365837.790 | 0.000 |
| 16 | 1 | 15 | 16.5 | 15 | 1 | 14 | 15.5 |  |  | 365871.940 | 0.052 |
| 17 | 1 | 17 | 16.5 | 16 | 1 | 16 | 15.5 | 439992.323 | 0.000 |  |  |
| 17 | 1 | 17 | 17.5 | 16 | 1 | 16 | 16.5 | 440030.728 | 0.009 |  |  |
| 17 | 7 | 11 | 16.5 | 16 | 7 | 10 | 15.5 | 440831.733 | 0.070 |  |  |
| 17 | 7 | 10 | 16.5 | 16 | 7 | 9 | 15.5 | 440831.733 | 0.070 |  |  |
| 17 | 7 | 11 | 17.5 | 16 | 7 | 10 | 16.5 | 440872.912 | -0.029 |  |  |
| 17 | 7 | 10 | 17.5 | 16 | 7 | 9 | 16.5 | 440872.912 | -0.029 |  |  |
| 17 | 5 | 13 | 16.5 | 16 | 5 | 12 | 15.5 | 442579.530 | 0.069 |  |  |
| 17 | 5 | 12 | 16.5 | 16 | 5 | 11 | 15.5 | 442579.530 | 0.069 |  |  |
| 17 | 5 | 13 | 17.5 | 16 | 5 | 12 | 16.5 | 442619.572 | 0.027 |  |  |
| 17 | 5 | 12 | 17.5 | 16 | 5 | 11 | 16.5 | 442619.572 | 0.027 |  |  |
| 17 | 4 | 14 | 16.5 | 16 | 4 | 13 | 15.5 | 443179.612 | -0.040 |  |  |
| 17 | 4 | 13 | 16.5 | 16 | 4 | 12 | 15.5 | 443179.612 | -0.048 |  |  |
| 17 | 4 | 14 | 17.5 | 16 | 4 | 13 | 16.5 | 443219.208 | -0.083 |  |  |
| 17 | 4 | 13 | 17.5 | 16 | 4 | 12 | 16.5 | 443219.208 | -0.091 |  |  |
| 17 |  | 15 | 16.5 | 16 | 3 | 14 | 15.5 | 443649.708 | 0.043 |  |  |
| 17 | 3 | 14 | 16.5 | 16 | 3 | 13 | 15.5 | 443652.831 | 0.172 |  |  |
| 17 | 3 | 15 | 17.5 | 16 | 3 | 14 | 16.5 | 443688.981 | 0.019 |  |  |
| 17 | 3 | 14 | 17.5 | 16 | 3 | 13 | 16.5 | 443691.996 | 0.038 |  |  |
| 17 | 0 | 17 | 16.5 | 16 | 0 | 16 | 15.5 | 443796.197 | 0.010 |  |  |
| 17 | 0 | 17 | 17.5 | 16 | 0 | 16 | 16.5 | 443834.896 | 0.004 |  |  |
| 17 | 2 | 16 | 16.5 | 16 | 2 | 15 | 15.5 | 443863.067 | -0.032 |  |  |
| 17 | 2 | 16 | 17.5 | 16 | 2 | 15 | 16.5 | 443902.148 | 0.038 |  |  |
| 17 | 2 | 15 | 16.5 | 16 | 2 | 14 | 15.5 | 444231.476 | 0.006 |  |  |
| 17 | 2 | 15 | 17.5 | 16 | 2 | 14 | 16.5 | 444270.608 | -0.001 |  |  |
| 17 | 1 | 16 | 16.5 | 16 | . 1 | 15 | 15.5 | 448040.351 | -0.028 |  |  |
| 17 | 1 | 16 | 17.5 | 16 | 1 | 15 | 16.5 | 448079.702 | 0.018 |  |  |
| 18 | 1 | 18 | 17.5 | 17 | 1 | 17 | 16.5 | 465811.623 | 0.014 |  |  |
| 18 | 1 | 18 | 18.5 | 17 | 1 | 17 | 17.5 | 465849.949 | -0.047 |  |  |
| 18 | 7 | 12 | 17.5 | 17 | 7 | 11 | 16.5 | 466715.621 | 0.059 |  |  |
| 18 | 7 | 11 | 17.5 | 17 | 7 | 10 | 16.5 | 466715.621 | 0.059 |  |  |
| 18 | 7 | 12 | 18.5 | 17 | 7 | 11 | 17.5 | 466756.529 | -0.047 |  |  |

Supplemental Table 1 com.

| N | $\mathrm{K}_{3}{ }^{\text {²}}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | J | N" | $\mathrm{K}_{\mathrm{s}}{ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $\mathrm{J}^{*}$ | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {obs }}$ | $v_{\text {orc }}$ | $V_{\text {obs }}$ | $v_{\text {osc }}$ |
| 18 | 7 | 11 | 18.5 | 17 | 7 | 10 | 17.5 | 466756.529 | -0.047 |  |  |
| 18 | 5 | 14 | 17.5 | 17 | 5 | 13 | 16.5 | 468564.467 | 0.064 |  |  |
| 18 | 5 | 13 | 17.5 | 17 | 5 | 12 | 16.5 | 468564.467 | 0.064 |  |  |
| 18 | 5 | 14 | 18.5 | 17 | 5 | 13 | 17.5 | 468604.343 | -0.010 |  |  |
| 18 | 5 | 13 | 18.5 | 17 | 5 | 12 | 17.5 | 468604.343 | -0.010 |  |  |
| 18 | 4 | 15 | 17.5 | 17 | 4 | 14 | 16.5 | 469200.306 | 0.000 |  |  |
| 18 | 4 | 14 | 17.5 | 17 | 4 | 13 | 16.5 | 469200.306 | -0.013 |  |  |
| 18 | 4. | 15 | 18.5 | 17 | 4 | 14 | 17.5 | 469239.805 | -0.055 |  |  |
| 18 | 4 | 14 | 18.5 | 17 | 4 | 13 | 17.5 | 469239.805 | -0.068 |  |  |
| 18 | 3 | 16 | 17.5 | 17 | 3 | 15 | 16.5 | 469699.918 | 0.108 |  |  |
| 18 | 3 | 15 | 17.5 | 17 | 3 | 14 | 16.5 | 469703.893 | 0.093 |  |  |
| 18 | 3 | 16 | 18.5 | 17 | 3 | 15 | 17.5 | 469739.072 | 0.012 |  |  |
| 18 | 3 | 15 | 18.5 | 17 | 3 | 14 | 17.5 | 469743.071 | 0.019 |  |  |
| 18 | 0 | 18 | 17.5 | 17 | 0 | 17 | 16.5 | 469800.629 | 0.016 |  |  |
| 18 | 0 | 18 | 18.5 | 17 | 0 | 17 | 17.5 | 469839.285 | -0.017 |  |  |
| 18 | 2 | 17 | 17.5 | 17 | 2 | 16 | 16.5 | 469912.317 | 0.070 |  |  |
| 18 | 2 | 17 | 18.5 | 17 | 2 | 16 | 17.5 | 469951.199 | -0.035 |  |  |
| 18 | 2 | 16 | 17.5 | 17 | 2 | 15 | 16.5 | 470349.284 | 0.042 |  |  |
| 18 | 2 | 16 | 18.5 | 17 | 2 | 15 | 17.5 | 470388.269 | -0.103 |  |  |
| 18 | , | 17 | 17.5 | 17 | 1 | 16 | 16.5 | 474327.816 | -0.031 |  |  |
| 18 | 1 | 17 | 18.5 | 17 | , | 16 | 17.5 | 474367.134 | -0.008 |  |  |
| 19 | , | 19 | 18.5 | 18 | 1 | 18 | 17.5 | 491620.034 | 0.000 | 421079.641 | 0.005 |
| 19 | 1 | 19 | 19.5 | 18 | 1 | 18 | 18.5 | 491658.388 | -0.025 | 421112.475 | 0.011 |
| 19 | 7 | 13 | 18.5 | 18 | 7 | 12 | 17.5 | 492591.148 | 0.066 | 426065.593 | 0.001 |
| 19 | 7 | 13 | 19.5 | 18 | 7 | 12 | 18.5 | 492631.844 | -0.028 | 426101.913 | -0.016 |
| 19 | 7 | 12 | 18.5 | 18 | 7 | 11 | 17.5 | 492591.148 | 0.066 | 426065.593 | 0.001 |
| 19 | 7 | 12 | 19.5 | 18 | 7 | 11 | 18.5 | 492631.844 | -0.028 | 426101.913 | -0.016 |
| 19 | 6 | 14 | 18.5 | 18 | 6 | 13 | 17.5 |  |  | 426679.769 | 0.007 |
| 19 | 6 | 14 | 19.5 | 18 | 6 | 13 | 18.5 |  |  | 426715.338 | -0.026 |
| 19 | 6 | 13 | 18.5 | 18 | 6 | 12 | 17.5 |  |  | 426679.769 | 0.007 |
| 19 | 6 | 13 | 19.5 | 18 | 6 | 12 | 18.5 |  |  | 426715.338 | -0.026 |
| 19 | 5 | 15 | 18.5 | 18 | 5 | 14 | 17.5 | 494540.745 | 0.054 | 427206.702 | -0.051 |
| 19 | 5 | 15 | 19.5 | 18 | 5 | 14 | 18.5 | 494580.486 | -0.042 | 427241.674 | -0.062 |
| 19 | 5 | 14 | 18.5 | 18 | 5 | 13 | 17.5 | 494540.745 | 0.054 | 427206.702 | -0.056 |
| 19 | 5 | 14 | 19.5 | 18 | 5 | 13 | 18.5 | 494580.486 | -0.042 | 427241.674 | -0.067 |
| 19 | 4 | 16 | 18.5 | 18 | 4 | 15 | 17.5 | 495212.415 | 0.029 |  |  |
| 19 | 4 | 16 | 19.5 | 18 | 4 | 15 | 18.5 | 495251.820 | -0.048 |  |  |
| 19 | 4 | 15 | 18.5 | 18 | 4 | 14 | 17.5 | 495212.415 | 0.010 |  |  |
| 19 | 4 | 15 | 19.5 | 18 | 4 | 14 | 18.5 | 495251.820 | -0.067 |  |  |
| 19 | 3 | 17 | 18.5 | 18 | 3 | 16 | 17.5 | 495741.680 | 0.031 | 428077.169 | -0.095 |
| 19 | 3 | 17 | 19.5 | 18 | 3 | 16 | 18.5 | 495780.804 | -0.056 | 428111.290 | -0.082 |
| 19 | 3 | 16 | 18.5 | 18 | 3 | 15 | 17.5 | 495746.979 | 0.097 | 428148.859 | -0.050 |
| 19 | 3 | 16 | 19.5 | 18 | 3 | 15 | 18.5 | 495786.090 | -0.006 |  |  |
| 19 | 0 | 19 | 18.5 | 18 | 0 | 18 | 17.5 | 495787.733 | 0.102 | 425980.808 | -0.015 |

Supplemental Table 1 cone.

| N | $\mathrm{K}_{3}{ }^{\circ}$ | $\mathrm{K}_{c}{ }^{\text {c }}$ | $J$ | $\mathrm{N}^{\text {w }}$ | $\mathbf{K}^{\prime \prime}$ | $\mathrm{K}_{8}{ }^{n}$ | J" | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{3}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {cos }}$ | $V_{0-G}$ | $V_{\text {cobs }}$ | $V_{0-6}$ |
| 19 | 0 | 19 | 19.5 | 18 | 0 | 18 | 18.5 | 495826.273 | -0.031 | 426013.794 | 0.061 |
| 19 | 2 | 18 | 18.5 | 18 | 2 | 17 | 17.5 | 495950.841 | -0.001 | 427676.599 | 0.026 |
| 19 | 2 | 18 | 19.5 | 18 | 2 | 17 | 18.5 | 495989.785 | -0.022 | 427710.277 | 0.054 |
| 19 | 2 | 17 | 18.5 | 18 | 2 | 16 | 17.5 | 496464.383 | 0.015 | 429891.309 | -0.005 |
| 19 | 2 | 17 | 19.5 | 18 | 2 | 16 | 18.5 | 496503.481 | -0.012 |  |  |
| 19 | 1 | 18 | 18.5 | 18 | 1 | 17 | 17.5 | 500603.453 | 0.009 |  |  |
| 19 | 1 | 18 | 19.5 | 18 | 1 | 17 | 18.5 | 500642.704 | -0.027 |  |  |
| 20 | 1 | 20 | 19.5 | 19 | 1 | 19 | 18.5 | 517417.008 | -0.004 | 443143.798 | 0.016 |
| 20 | 1 | 20 | 20.5 | 19 | 1 | 19 | 19.5 | $\$ 17455.315$ | -0.068 | 443176.642 | 0.052 |
| 20 | 0 | 20 | 19.5 | 19 | 0 | 19 | 18.5 | \$21756.320 | -0.004 | 448117.214 | 0.018 |
| 20 | 0 | 20 | 20.5 | 19 | 0 | 19 | 19.5 | \$21794.944 | -0.036 | 448150.082 | 0.030 |
| 20 | 7 | 14 | 19.5 | 19 | 7 | 13 | 18.5 | 518457.801 | 0.039 | 448454.592 | 0.045 |
| 20 | 7 | 14 | 20.5 | 19 | 7 | 13 | 19.5 | 518498.252 | -0.109 | 448490.628 | 0.015 |
| 20 | 7 | 13 | 19.5 | 19 | 7 | 12 | 18.5 | 518457.801 | 0.039 | 448454.592 | 0.045 |
| 20 | 7 | 13 | 20.5 | 19 | 7 | 12 | 19.5 | 518498.252 | -0.109 | 448490.628 | 0.015 |
| 20 | 6 | 15 | 19.5 | 19 | 6 | 14 | 18.5 |  |  | 449102.147 | 0.016 |
| 20 | 6 | 15 | 20.5 | 19 | 6 | 14 | 19.5 |  |  | 449137.528 | -0.007 |
| 20 | 6 | 14 | 19.5 | 19 | 6 | 13 | 18.5 |  |  | 449102.147 | 0.015 |
| 20 | 6 | 14 | 20.5 | 19 | 6 | 13 | 19.5 |  |  | 449137.528 | -0.007 |
| 20 | 5 | 16 | 19.5 | 19 | 5 | 15 | 18.5 | 520507.863 | 0.016 | 449659.531 | 0.022 |
| 20 | 5 | 16 | 20.5 | 19 | 5 | 15 | 19.5 | 520547.481 | -0.106 | 449694.338 | -0.017 |
| 20 | 5 | 15 | 19.5 | 19 | 5 | 14 | 18.5 | 520507.863 | 0.016 | 449659.531 | 0.014 |
| 20 | 5 | 15 | 20.5 | 19 | 5 | 14 | 19.5 | 520547.481 | -0.106 | 449694.338 | -0.025 |
| 20 | 2 | 19 | 19.5 | 19 | 2 | 18 | 18.5 | 521978.335 | 0.035 | 450099.644 | 0.052 |
| 20 | 2 | 19 | 20.5 | 19 | 2 | 18 | 19.5 | 522017.138 | -0.110 | 450133.264 | 0.056 |
| 20 | 4 | 17 | 19.5 | 19 | 4 | 16 | 18.5 | 521215.392 | -0.051 | 450149.228 | -0.025 |
| 20 | 4 | 17 | 20.5 | 19 | 4 | 16 | 19.5 | 521254.758 | -0.078 | 450183.631 | -0.023 |
| 20 | 4 | 16 | 19.5 | 19 | 4 | 15 | 18.5 | 521215.392 | -0.051 | 450150.614 | 0.126 |
| 20 | 4 | 16 | 20.5 | 19 | 4 | 15 | 19.5 | 521254.758 | -0.078 | 450184.941 | 0.051 |
| 20 | 3 | 18 | 19.5 | 19 | 3 | 17 | 18.5 | 521774.735 | 0.029 | 450588.085 | -0.041 |
| 20 | 3 | 18 | 20.5 | 19 | 3 | 17 | 19.5 | 521813.860 | -0.023 | 450622.131 | -0.058 |
| 20 | 3 | 17 | 19.5 | 19 | 3 | 16 | 18.5 | 521781.557 | 0.084 | 450680.809 | 0.076 |
| 20 | 3 | 17 | 20.5 | 19 | 3 | 16 | 19.5 | 521820.684 | 0.030 | 450714.910 | 0.071 |
| 20 | 2 | 18 | 19.5 | 19 | 2 | 17 | 18.5 | 522576.656 | 0.003 | 452667.527 | . 0.021 |
| 20 | 2 | 18 | 20.5 | 19 | 2 | 17 | 19.5 | 522615.781 | 0.004 | 452701.824 | -0.011 |
| 20 | , | 19 | 19.5 | 19 | 1 | 18 | 18.5 | 526866.469 | -0.031 | 456853.720 | 0.035 |
| 20 | 1 | 19 | 20.5 | 19 | 1 | 18 | 19.5 | 526905.752 | -0.026 | 456887.695 | 0.019 |
| 21 | 1 | 21 | 20.5 | 20 | 1 | 20 | 19.5 |  |  | 465193.666 | -0.030 |
| 21 | 1 | 21 | 21.5 | 20 | 1 | 20 | 20.5 |  |  | 465226.492 | 0.007 |
| 21 | 0 | 21 | 20.5 | 20 | 0 | 20 | 19.5 |  |  | 470214.794 | 0.018 |
| 21 | 0 | 21 | 21.5 | 20 | 0 | 20 | 20.5 |  |  | 470247.589 | 0.014 |
| 21 | 7 | 15 | 20.5 | 20 | 7 | 14 | 19.5 |  |  | 470837.862 | 0.037 |
| 21 | 7 | 15 | 21.5 | 20 | 7 | 14 | 20.5 |  |  | 470873.656 | -0.002 |
| 21 | 7 | 14 | 20.5 | 20 | 7 | 13 | 19.5 |  |  | 470837.862 | 0.037 |

Supplemental Table 1 cont.

| N | K ${ }^{\prime}$ | $\mathbf{K}_{\text {c }}{ }^{\prime}$ | J | N" | K ${ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $\mathrm{J}^{n}$ | $\mathrm{MgNH}_{2}$ | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {obs }} \quad v_{\text {ose }}$ | $v_{\text {cts }}$ | $v_{\text {ors }}$ |
| 21 | 7 | 14 | 21.5 | 20 | 7 | 13 | 20.5 |  | 470873.656 | -0.002 |
| 21 | 6 | 16 | 20.5 | 20 | 6 | 15 | 19.5 |  | 471519.023 | 0.018 |
| 21 | 6 | 16 | 21.5 | 20 | 6 | 15 | 20.5 |  | 471554.214 | -0.023 |
| 21 | 6 | 15 | 20.5 | 20 | 6 | 14 | 19.5 |  | 471519.023 | 0.018 |
| 21 | 6 | 15 | 21.5 | 20 | 6 | 14 | 20.5 |  | 471554.214 | -0.023 |
| 21 | 5 | 17 | 20.5 | 20 | 5 | 16 | 19.5 |  | 472107.195 | 0.008 |
| 21 | 5 | 17 | 21.5 | 20 | 5 | 16 | 20.5 |  | 472141.913 | -0.004 |
| 21 | 5 | 16 | 20.5 | 20 | 5 | 15 | 19.5 |  | 472107.195 | -0.005 |
| 21 | 5 | 16 | 21.5 | 20 | 5 | 15 | 20.5 |  | 472141.913 | -0.017 |
| 21 | 2 | 20 | 20.5 | 20 | 2 | 19 | 19.5 |  | 472509.300 | 0.038 |
| 21 | 2 | 20 | 21.5 | 20 | 2 | 19 | 20.5 |  | 472542.892 | 0.045 |
| 21 | 4 | 18 | 20.5 | 20 | 4 | 17 | 19.5 |  | 472627.702 | -0.049 |
| 21 | 4 | 18 | 21.5 | 20 | 4 | 17 | 20.5 |  | 472661.992 | -0.089 |
| 21 | 4 | 17 | 20.5 | 20 | 4 | 16 | 19.5 |  | 472629.588 | 0.094 |
| 21 | 4 | 17 | 21.5 | 20 | 4 | 16 | 20.5 |  | 472663.891 | 0.066 |
| 21 | 3 | 19 | 20.5 | 20 | 3 | 18 | 19.5 |  | 473094.829 | -0.058 |
| 21 | 3 | 19 | 21.5 | 20 | 3 | 18 | 20.5 |  | 473128.809 | -0.103 |
| 21 | 3 | 18 | 20.5 | 20 | 3 | 17 | 19.5 |  | 473213.144 | 0.085 |
| 21 | 3 | 18 | 21.5 | 20 | 3 | 17 | 20.5 |  | 473247.229 | 0.093 |
| 21 | 2 | 19 | 20.5 | 20 | 2 | 18 | 19.5 |  | 475461.818 | 0.040 |
| 21 | 2 | 19 | 21.5 | 20 | 2 | 18 | 20.5 |  | 475496.040 | -0.052 |
| 21 | 1 | 20 | 20.5 | 20 | 1 | 19 | 19.5 |  | 479561.084 | 0.034 |
| 21 | 1 | 20 | 21.5 | 20 | 1 | 19 | 20.5 |  | 479594.997 | -0.016 |
| 22 |  | 22 | 21.5 | 21 | 1 | 21 | 20.5 |  | 487228.919 | 0.023 |
| 22 | 1 | 22 | 22.5 | 21 | 1 | 21 | 21.5 |  | 487261.655 | -0.011 |
| 22 | 0 | 22 | 21.5 | 21 | 0 | 21 | 20.5 |  | 492273.196 | -0.025 |
| 22 | 0 | 22 | 22.5 | 21 | 0 | 21 | 21.5 |  | 492305.923 | -0.039 |
| 22 | 7 | 16 | 21.5 | 21 | 7 | 15 | 20.5 |  | 493215.184 | 0.039 |
| 22 | 7 | 16 | 22.5 | 21 | 7 | 15 | 21.5 |  | 493250.725 | -0.051 |
| 22 | 7 | 15 | 21.5 | 21 | 7 | 14 | 20.5 |  | 493215.184 | 0.039 |
| 22 | 7 | 15 | 22.5 | 21 | 7 | 14 | 21.5 |  | 493250.725 | -0.051 |
| 22 | 6 | 17 | 21.5 | 21 | 6 | 16 | 20.5 |  | 493930.135 | 0.029 |
| 22 | 6 | 17 | 22.5 | 21 | 6 | 16 | 21.5 |  | 493965.163 | -0.028 |
| 22 | 6 | 16 | 21.5 | 21 | 6 | 15 | 20.5 |  | 493930.135 | 0.029 |
| 22 | 6 | 16 | 22.5 | 21 | 6 | 15 | 21.5 |  | 493965.163 | -0.028 |
| 22 | 5 | 18 | 21.5 | 21 | 5 | 17 | 20.5 |  | 494549.576 | 0.043 |
| 22 | 5 | 18 | 22.5 | 21 | 5 | 17 | 21.5 |  | 494584.158 | -0.005 |
| 22 | 5 | 17 | 21.5 | 21 | 5 | 16 | 20.5 |  | 494549.576 | 0.023 |
| 22 | 5 | 17 | 22.5 | 21 | 5 | 16 | 21.5 |  | 494584.158 | -0.024 |
| 22 | 2 | 21 | 21.5 | 21 | 2 | 20 | 20.5 |  | 494904.946 | 0.010 |
| 22 | 2 | 21 | 22.5 | 21 | 2 | 20 | 21.5 |  | 494938.495 | 0.004 |
| 22 | 4 | 19 | 21.5 | 21 |  | 18 | 20.5 |  | 495101.816 | 0.011 |
| 22 | 4 | 19 | 22.5 | 21 | 4 | 18 | 21.5 |  | 495136.063 | -0.010 |
| 22 | 4 | 18 | 21.5 | 21 | 4 | 17 | 20.5 |  | 495104.247 | 0.022 |

Supplemental Table 1 cont.

| N | $\mathrm{K}_{\mathrm{a}}{ }^{\prime}$ | Ks' | $J$ | $\mathrm{N}^{*}$ | $\mathrm{K}_{\mathrm{a}}{ }^{\prime \prime}$ | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | J" | $\mathrm{MgNH}_{2}$ |  | $\mathrm{MgND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  | $v_{\text {obs }}$ | $v_{\text {ore }}$ | $v_{\text {obs }}$ | $v_{\text {ors }}$ |
| 22 | 4 | 18 | 22.5 | 21 | 4 | 17 | 21.5 |  |  | 495138.478 | -0.016 |
| 22 | 3 | 20 | 21.5 | 21 | 3 | 19 | 20.5 |  |  | 495597.021 | -0.096 |
| 22 | 3 | 20 | 22.5 | 21 | 3 | 19 | 21.5 |  |  | 495630.979 | -0.130 |
| 22 | 3 | 19 | 21.5 | 21 | 3 | 18 | 20.5 |  |  | 495746.275 | 0.116 |
| 22 | 3 | 19 | 22.5 | 21 | 3 | 18 | 21.5 |  |  | 495780.286 | 0.072 |
| 22 | 2 | 20 | 21.5 | 21 | 2 | 19 | 20.5 |  |  | 498273.321 | 0.027 |
| 22 | 2 | 20 | 22.5 | 21 | 2 | 19 | 21.5 |  |  | 498307.635 | -0.001 |
| 22 | 1 | 21 | 21.5 | 21 | 1 | 20 | 20.5 |  |  | 502247.352 | 0.002 |
| 22 | 1 | 21 | 22.5 | 21 | 1 | 20 | 21.5 |  |  | 502281.251 | -0.032 |
| 23 | 1 | 23 | 22.5 | 22 | 1 | 22 | 21.5 |  |  | 509248.963 | 0.036 |
| 23 | 1 | 23 | 23.5 | 22 | 1 | 22 | 22.5 |  |  | 509281.625 | -0.054 |
| 23 | 0 | 23 | 22.5 | 22 | 0 | 22 | 21.5 |  |  | 514292.476 | -0.009 |
| 23 | 0 | 23 | 23.5 | 22 | 0 | 22 | 22.5 |  |  | 514325.129 | -0.040 |
| 23 | 7 | 17 | 22.5 | 22 | 7 | 16 | 21.5 |  |  | 515586.212 | -0.008 |
| 23 | 7 | 17 | 23.5 | 22 | 7 | 16 | 22.5 |  |  | 515621.657 | -0.018 |
| 23 | 7 | 16 | 22.5 | 22 | 7 | 15 | 21.5 |  |  | 515586.212 | -0.008 |
| 23 | 7 | 16 | 23.5 | 22 | 7 | 15 | 22.5 |  |  | 515621.657 | -0.018 |
| 23 | 6 | 18 | 22.5 | 22 | 6 | 17 | 21.5 |  |  | 516335.190 | 0.031 |
| 23 | 6 | 18 | 23.5 | 22 | 6 | 17 | 22.5 |  |  | 516370.085 | -0.031 |
| 23 | 6 | 17 | 22.5 | 22 | 6 | 16 | 21.5 |  |  | 516335.190 | 0.031 |
| 23 | 6 | 17 | 23.5 | 22 | 6 | 16 | 22.5 |  |  | 516370.085 | -0.031 |
| 23 | 5 | 19 | 22.5 | 22 | 5 | 18 | 21.5 |  |  | 516986.337 | 0.047 |
| 23 | 5 | 19 | 23.5 | 22 | 5 | 18 | 22.5 |  |  | 517020.816 | -0.016 |
| 23 | 5 | 18 | 22.5 | 22 | 5 | 17 | 21.5 |  |  | 516986.337 | 0.018 |
| 23 | 5 | 18 | 23.5 | 22 | 5 | 17 | 22.5 |  |  | 517020.816 | -0.045 |
| 23 | 2 | 22 | 22.5 | 22 | 2 | 21 | 21.5 |  |  | 517285.953 | -0.017 |
| 23 | 2 | 22 | 23.5 | 22 | 2 | 21 | 22.5 |  |  | 517319.432 | -0.066 |
| 23 | 4 | 20 | 22.5 | 22 | 4 | 19 | 21.5 |  |  | 517571.214 | 0.031 |
| 23 | 4 | 20 | 23.5 | 22 | 4 | 19 | 22.5 |  |  | 517605.396 | -0.003 |
| 23 | 4 | 19 | 22.5 | 22 | 4 | 18 | 21.5 |  |  | 517574.527 | 0.036 |
| 23 | 4 | 19 | 23.5 | 22 | 4 | 18 | 22.5 |  |  | 517608.668 | -0.041 |
| 23 | 3 | 21 | 22.5 | 22 | 3 | 20 | 21.5 |  |  | 518094.237 | -0.122 |
| 23 | 3 | 21 | 23.5 | 22 | 3 | 20 | 22.5 |  |  | 518128.163 | -0.160 |
| 23 | 3 | 20 | 22.5 | 22 | 3 | 19 | 21.5 |  |  | 518280.398 | 0.059 |
| 23 | 3 | 20 | 23.5 | 22 | 3 | 19 | 22.5 |  |  | 518314.593 | 0.215 |
| 23 | 2 | 21 | 22.5 | 22 | 2 | 20 | 21.5 |  |  | 521101.147 | 0.058 |
| 23 | 2 | 21 | 23.5 | 22 | 2 | 20 | 22.5 |  |  | 521135.437 | -0.023 |
| 23 | 1 | 22 | 22.5 | 22 | 1 | 21 | 21.5 |  |  | 524911.269 | -0.047 |
| 23 | 1 | 22 | 23.5 | 22 | 1 | 21 | 22.5 |  |  | 524945.180 | -0.039 |

a) $\ln \mathrm{MHz}$.

## APPENDIX D

FIRST SYNTHESIS AND STRUCTURAL DETERMINATION OF A MONOMERIC, UNSOLVATED LITHIUM AMIDE, $\mathrm{LiNH}_{2}$
D. B. Grotjahn, P. M. Sheridan, I. Al-Jihad, and L. M. Ziurys, J. Am. Chem. Soc. 123, 5489-5494 (2001).

# First Synthesis and Structural Determination of a Monomeric, Unsolvated Lithium Amide, $\mathrm{LiNH}_{2}$ 

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#### Abstract

Alkali metal amides typically ageregate in solution and the solid phase, and even in the gas phase. In addition, even in the few known monomeric structures, the coordination number of the alkali metal is raised by binding of Lewis-basic solvent molecules, with concomitant changes in structure. In convast. the simplest lizhium amide $\mathrm{LiNH}_{2}$ has never been made in a monomeric form, even though its structure has been theoretically predicted several imes. Here, the first experimental structural data for a monomeric, unsolvated lithum amide are determined using a combination of gas-phase synthesis and millimeter/submillimerer-wave spectroscopy. All data point to a planar structure for $\mathrm{LiNH}_{2}$. The $\mathrm{r}_{0}$ structure of $\mathrm{LiNH}_{2}$ has a $\mathrm{Li}-\mathrm{N}$ distance of $1.736(3) \AA$, an $\mathrm{N}-\mathrm{H}$ distance of $1.022(3) \mathrm{A}$. and a $\mathrm{H}-\mathrm{N}-\mathrm{H}$ angle of $106.9(1)^{\circ}$. These results are compared with theoretical predictions for $\mathrm{LiNH}_{2}$, and experimental data for oligomeric, solid-phase samples, which could not resolve the question of whether $\mathrm{LiNH}_{2}$ is planar or not. In addition, comparisons are made with revised gas-phase and solid-phase data and calculated structures of $\mathrm{NaNH}_{2}$.


## Infroduction

Alkali metal amides have played a promineat role in the development of chemistry as a science. ${ }^{i m 4}$ Sodium and potassium amide were first reported at the beginning of the 19 th cennry by Gay-Lussac and Thenard and independently by Davy, who used the new substances to reach conclusions about the constitutions of sodium, potassium, and ammonia.' Lithium amide was first made at the end of the last century. ${ }^{5}$ The threedimensional structures of solid alkali metal amides were first examined by $\mathbb{R}$ spectroscopy ${ }^{6}$ and NMR spectroscopy in the 1950 . $^{7}$ In addition. X-ray crystallographys ${ }^{-10}$ showed the distorted cubic close-packing of amide amions and the presence of alkali cations in tetrahedral holes between the anions. Thus, each ion is associated with several ions of the opposite charge. Later refinement of the crystal strucnure of $\mathrm{LiNH}_{2}{ }^{11}$ suggested that the variation in orienration of $\mathrm{NH}_{2}$ groups in the crystal is dictased by the packing of the jons in the unit cell, making it impossible to form conclusions about the structure of the bypotbetical monomer. Continuing this theme, derivatives of lithium amide with substituents on the nitrogen show a beautiful variery of aggregated strucruses both in the solid state and in

[^3]solution, ${ }^{12-18}$ with hexagonal prisms, ladders, and other evocative names used to describe the architecnures seen. In fact, only a handful of crystallographically characterized monomeric lithium amides are known; ${ }^{1214-17}$ three examples are shown in Scheme $1 .{ }^{19-21}$ These unusial structures, all featuring solvent molecule(s) such as THF or amines coordinated to lithium, are the result of employing sterically demanding and/or electronically stabilizing substituents at the anionic nitrogen of the amide ligand. In contrast. meither monomeric lithium nor sodium amide is known, although the lithium compound has been proposed (without direct evidence) to have been generated in an argon marrix by irradiating a lithium-ammonia adduct. ${ }^{72}$ Compurational studies of Jithium amide as a protorypical alkali metal amide have focused on dimers, ${ }^{2324}$ trimers, ${ }^{24}$ retramers, ${ }^{25}$ or hexamers. ${ }^{26}$
Lithium and sodium amide became imporant reagents in organic synthesis, rather than laboratory curiosinies, becsuse they were found to deprosonate ketones. aldehydes, and structurally

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Scheme

1
1.895(8) A shortest LiN bond to date

3
LiN $4.959(7)$ A
related organic molecules. ${ }^{27-32}$ Sodium amide has been described as leading to the birth of strong-base chemistry. ${ }^{4}$ Depending on the application, either lithium amide ${ }^{33.34}$ or sodium amide ${ }^{35.36}$ has been found to be superior.
The use of large groups on the amide nitrogen frequently results in regioselective and stereoselective deprotonation in reactions umder kinetic control. ${ }^{28}$ The enolates so produced are versatile species in organic synthesis, for example, as precursors to regio- and stereodefined enolates of silicon, boron, or other elements, which in turn can control subsequent carbon-carbon bond-forming reactions. Recent developments in alkali metal amide chemistry have focused on the use of chiral amides for processes such as deprotonation ${ }^{37-39}$ or reduction ${ }^{40}$ If a synthetic chemist wishes to reverse a $10: 1$ ratio of products to $1: 10$, at $-78{ }^{\circ} \mathrm{C}$, a common temperature for use of alkali metal amides, a change in $\Delta G^{*}$ for two altemate transinion states of only 1.8

[^4]$\mathrm{kcal}^{\mathrm{mol}}{ }^{-1}$ is required. Clearly, a subtle change in structure (e.g., bond lengths and anglesi could lead to dramatic change in the free energy changes involved, and bence a sharp reversal of selectivity. Theoretical calculations anempting to model subtle structural feanores will rely on comparisons of calculated strucures for simpler molecules with precise experimenal data such as those provided in this paper.
Regardless of the specific application, understanding the structure of the alkali amides is crucial to controlling selectivity. Elegans and difficult studies by the groups of Collum. ${ }^{13}$ Hilmersson and Davidsson, ${ }^{41.42}$ Klumpp, ${ }^{43}$ and ohers are elucidating the solution structures of lithium amides. However, because solution structure studies do not give information about bond lengths and angies, only on arom connectivity and equilibria between species. other techniques are needed to compare theoretical and actual geometries. In this paper we repon the first synthesis of an unsolvased, monomeric lithium amide, $\mathrm{LiNH}_{2}$. This is possible only in the gas phase, where millimeter/submillimeter spectroscopy was used to precisely determine bond lemgths and angles. Precise experimental data on the boad lepgths and angles of gas-phase monomers will allow refinement of theoretical calculations. The data presented bere are the first available for $\mathrm{LiNH}_{2}$, a key model compound for larger amides used in synthesis.

## Experimental Section

The pure rotational spectra of $\mathrm{LiNH}_{2}$ and $\mathrm{LiND}_{2}$ were measured using m millimeter/submillimeter-wave absorption spectrometer. parts of which are described elsewbere in detail. ${ }^{44}$ Briefly. the source of tunable millimeter-wave radiation is a phase-locked Gunn oscillator used in conjunction with a Schotky diode muhtiplier. Several Gunn oscillators and multipliers are necessary to cover the frequency range of $100-$ 550 GHz . The radiation is launched from a scalar feedhorn with a Gaussian beam shape and is passed through a wire polarizing grid. Using wo offset ellipsoidal mirrors. the radiation is quasioptically propagated through the reaction chamber, which is a double-pass system and is water-cooled. A roots-type blower pumping system continuously evacuares the cell. The molecules are created is this chamber which contanns a Broida-type oven. The oven is used waporize metals by resistive heating. A rooftop reflector at the back of the cell changes the polarization of the radiation by $90^{\circ}$ and reflects it back through the cell and mirror optics and into a liquid belium cooled InSb belomerer detector. The radiation source is frequency modutated at 25 kHz and data are recorded as second derivative spectra using a lock-in amplifier. The path leagth chrough the spectrometer system is additionally modulated using a movable rooftop reflector. located at the beam waist berween the two mirrors, to improve the baseline.

LiNH $H_{2}$ was synthesized in the gas phase by the reaction of lithimo and ammonie. with argon serving as the carrier gas. The lithium vapor was created by heatimg solid lithium in the Broida-iype oven. ${ }^{44}$ The lithinm vapor whas entrained is a $1: 1$ minture of ammonia and argon. added over the top of the oven. About 10 mTort of earh gas was used. The molecule was synchesized continuousiy in the reaction cell for as long as lithium vapor was present (1) io 2 b). Molecule lifetimes are estimated to be less than 1 a. For $\mathrm{LiND}_{2}$, the same procedure was
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followed. using $\mathrm{ND}_{3}$ rather than $\mathrm{NH}_{3}$. Lime intensities were typically weaker for the deuterated species.

Fizal transition frequency measurements were obtained from seans $5 \mathrm{MH} z$ in frequency coverage. One scan in increasing frequency and one in decreasing frequency were rypically averaged topether. For weaker lines. particularly at lower frequencies. the number of scams was increased to eight or twelve. All lize profiles were fila to Gaussian shapes to determine the center. Line widths ranged from 400 to 1400 kHz over 114-535 GHz.

## Results emd Discussian

Syathesis. Theoretical calculations suggested that vaporizing monomeric $\mathrm{LiNH}_{2}$ from the dimer. ${ }^{23,24}$ trimer, ${ }^{24}$ tetramer, ${ }^{25}$ or bexamer ${ }^{36}$ would be difficult if not impossible, a situation also enconntered in simple alkyllithinms such as $\mathrm{CH}_{3} \mathrm{Li}$, ${ }^{45}$ Therefore, rather than attempting to vaporize the monomer from a solidphase sample, we prepared $\mathrm{LiNH}_{2}$ or $\mathrm{LiND}_{2}$ directly in the gas phase by reaction of gaseous $\mathrm{NH}_{3}$ or $\mathrm{ND}_{3}$ and lithium vapor. A dic discharge was unnecessary, unlike in the previously reported symthesis of $\mathrm{NaNH}_{2}$ from ammonia and sodium. ${ }^{46}$ Details of the synthesis are foumd in the Experimental Section.

Analysis of the Data. Table I shows the observed transitions for both $\mathrm{LiNH}_{2}$ and $\mathrm{LiND}_{2}$. Assuming both isotopomers are near prolate asymmeric top species with $C_{2}$. symmery and ${ }^{1} A_{i}$ ground electronic states, the quantum numbers which describe the rotational transitions of this molecule are $J, K_{\mathrm{a}}$, and $K_{\text {e }} . J$ represents the total angular momentum of the molecule, exclusive of nuclear spin. $K_{\mathrm{a}}$ and $K_{c}$ are projections of $J$ onto the symmetry axis of the molecule in the respective prolate and oblate symmetric iop limits. In the case of an asymmetric iop, $K_{\text {a }}$ and $K_{c}$ are no longer well defined and serve only as energy level labels.

As described below, all evidence suggests that the molecule is planar; hence, the dipole moment only lies along the $a$-axis and rotational transitions follow a-type selection rules ( $\Delta K_{\mathrm{a}}=$ $0, \Delta K_{\mathrm{r}}= \pm 1$ ). Since $\Delta K_{\mathrm{s}}=0$, asymmery components can be labeled by the $K_{\mathrm{m}}$ quanrm mumber. In a low $J$ transition of a near prolate asymmetric top, the $K_{\mathrm{a}}=0$ component appears approximately at the center between the two asymmetrically split $K_{\mathrm{a}}=1$ components. Other $K_{\mathrm{a}}$ components progress lower in frequency from the $K_{a}=0$ component with decreased splitting. However, as $J$ increases, so does the asymmetry doubling. This results in the $K_{\mathrm{a}}=0$ component shifting lower in frequency, often lower than bigher $K_{2}$ components. This effect is also increased on deuteration, since the molecule becomes more asymmetric relative to the center of mass.

Identifying this asymmetric top patien was not trivial for $\mathrm{L} \mathrm{NH}_{2}$ or $\mathrm{LiND}_{2}$ because of the relatively large rotational constanis for these species. The initial search for $\mathrm{LiNH}_{2}$ began by searching 150 CHz of frequency space, which is approximately $6 B$ of the estimated rotational constant of 28-31 GHz , based on other alkaline-earth amide species. ${ }^{46} K_{2}$ components in adjacent transitions were identified by establishing harnonic relationships between lines fit with effective rotational constants in this range. Once several of these relaionships were defemined, preliminary assignment of the $\mathcal{K}_{t}$ quanimm number was made. This assignment was aided by the effect of nuclear spin statistics on the spectrum. $A C_{2}$ rotation of $\mathrm{LiNH} \mathrm{H}_{2}$ results in the exchange of the two protons, wich are fermions $(I=$ 1/2). The rotal wave function, which describes the molecule, must be anrisymuetric to this exchange. Thus, the ortho energy levels, which the odd $K_{3}$ componens arise from, have a degeneracy of
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Toble 1. Observed Transition Frequencies of LiNH, and LiND: $\left(X^{1} A_{1}\right)^{\prime}$

| $I$ | $R^{\text {R }}$ | $K_{E}^{\prime}$ | F | $K_{0}{ }^{\prime \prime}$ | $K^{*}$ | LiNH2 |  | $\mathrm{LiND}_{2}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  | $1{ }^{1}$ | $t$ - $\mathrm{icos}^{\text {a }}$ | 8 | $u_{0}$ |
| 2 | 1 | 2 | 1 | 1 | 1 | 114201.204 | -0.053 |  |  |
| 2 | 0 | 2 | 1 | 0 | 1 | 118584.439 | -0.032 |  |  |
| 4 | 1 | 4 | 3 | 1 | 3 | 228354.543 | -0.006 |  |  |
| 4 | 3 | 1 | 3 | 3 | 0 | 232238.839 | -0.172 |  |  |
| 4 | 3 | 2 | 3 | 3 | 1 | 2322388853 | 0.007 |  |  |
| 4 | 2 | 3 | 3 | 2 | 2 | 232738.999 | 0.038 |  |  |
| 4 | 2 | 2 | 3 | 2 | 1 | 232847.806 | -0.906 |  |  |
| 4 | 0 | 4 | 3 | 0 | 3 | 233050.121 | -0.037 |  |  |
| 4 | 1 | 3 | 3 | 1 | 2 | 237718.425 | 0.003 |  |  |
| 5 | 1 | 5 | 4 | 1 | 4 | 285398.338 | -0.007 |  |  |
| 3 | 4 | 2 | 4 | 4 | 1 | 289320.694 | -0.028 |  |  |
| 5 | 4 | 1 | 4 | 4 | 0 | 289320.694 | -0.028 |  |  |
| 5 | 2 | 4 | 4 | 2 | 3 | 290884.950 | 0.088 |  |  |
| 5 | 2 | 3 | 4 | 2 | 2 | 291102.497 | 0.004 |  |  |
| 5 | 0 | 5 | 4 | 0 | 4 | 291201.418 | -0.020 |  |  |
| 5 | 1 | 4 | 4 | 1 | 3 | 297097.236 | 0.020 |  |  |
| 6 | 1 | 6 | 5 | 1 | 5 | 342412.422 | -0.002 | 290701.606 | -0.037 |
| 6 | 5 | 2 | 5 | 5 | 1 | 345621.312 | -0.043 | 298974.311 | 0.041 |
| 6 | 5 | 1 | 5 | 5 | 0 | 345621.312 | -0.043 | 298974.311 | 0.040 |
| 6 | 4 | 3 | 5 | 4 | 2 | 347158.453 | 0.018 | 29989\%.615 | 0.036 |
| 6 | 4 | 2 | 5 | 4 | 1 | 347158.453 | 0.016 | 299896.615 | -0.075 |
| 6 | 3 | 4 | 5 | 3 | 3 | 348318.508 | -0.089 | 300663.792 | -0.083 |
| 6 | 3 | 3 | 5 | 3 | 2 | 348320.251 | -0.023 | 300687.971 | -0.031 |
| $\sigma$ | 2 | 5 | 5 | 2 | 4 | 349005.022 | 0.089 | 300672.097 | -0.039 |
| 6 | 0 | 6 | 5 | 0 | 5 | 349278.714 | -0.001 | 299548.872 | -0.064 |
| 6 | 2 | 4 | 5 | 2 | 3 | 349385.480 | 0.005 | 302366.461 | -0.041 |
| 6 | 1 | 5 | 5 | 1 | 4 | 356441.919 | -0.071 | 310847.718 | -0.051 |
| 7 | 1 | 7 | 6 | , | 6 | 399391.023 | 0.006 | 338952.389 | -0.007 |
| 7 | 6 | 2 | 6 | 6 | 1 |  |  | 347504.282 | 0.023 |
| 7 | 6 |  | 6 | 6 | 0 |  |  | 347504.282 | 0.023 |
| 7 | 5 | 3 | 6 | 5 | 2 |  |  | 348809.359 | 0.037 |
| 7 | 5 | 2 | 6 | 5 | 1 |  |  | 348809.359 | 0.036 |
| 7 | 4 | 4 | 6 | 4 | 3 | 404981.773 | 0.052 | 349901.743 | 0.165 |
| 7 | 4 | 3 | 6 | 4 | 2 | 40498i.773 | 0.044 | 349901.743 | -0.204 |
| 7 | 3 | 5 | 6 | 3 | 4 | 406341.204 | -0.015 | 350825.860 | -0.006 |
| 7 | 3 | 4 | 6 | 3 | 3 | 406344.942 | -0.050 | 350880.141 | 0.002 |
| 7 | 2 | 6 | 6 | 2 | 5 | 407094.058 | 0.106 | 350633.416 | 0.015 |
| 7 | 0 | 9 | 6 | 0 | 6 | 407267.422 | -0.007 | 348713.754 | 0.018 |
| 7 | 2 | 5 | 6 | 2 | 4 |  |  | 353329.057 | 0.009 |
| 7 | 1 | 6 | 6 | 1 | 5 | 415745.804 | 0.011 | 362417.626 | 0.029 |
| 8 | 1 | 8 | 7 |  | 7 | 456328.442 | -0.009 | 387116.838 | 0.047 |
| 8 | 6 | 3 | 7 | 6 | 2 |  |  | 397146.489 | -0.046 |
| 8 | 6 | 2 | 7 | 6 | 1 |  |  | 397146.489 | -0.046 |
| 8 | 5 | 4 | 7 | 5 | 3 | 460739.072 | 0.083 | 398647.068 | 0.019 |
| 8 | 5 | 3 | 7 | 5 | 2 | 460739.072 | 0.083 | 398647.068 | 0.014 |
| 8 | 4 | 9 | 7 | 4 | 4 | 452788.237 | 0.072 |  |  |
| 8 | 4 | 4 | 7 | 4 | 3 | 462788. 237 | 0.050 |  |  |
| 8 | 3 | 6 | 7 | 3 | 5 | 464349.347 | 0.008 | 401005.742 | 0.002 |
| 8 | 3 | 3 | 7 | 3 | 4 | 464356.889 | 0.007 | 401114.225 | 0.003 |
| 8 | 2 | 7 | 7 | 2 | 6 | 465146.843 | 0.060 | 4090525.148 | 0.027 |
| 8 | 0 | 8 | 7 | 0 | 7 | 465153.279 | 0.032 | 397547.572 | 0.057 |
| 8 | 2 | 6 | 7 | 2 | 5 | 466057.952 | 0.031 | 404533.928 | 0.037 |
| 8 | 1 | 7 | 7 | 1 | 6 | 475001.586 | -0.009 | 413871.289 | 0.020 |
| 9 | 1 | 9 | 8 | 1 | 8 | \$\$3219.097 | -0.066 |  |  |
| 9 | 6 | 4 | 8 | 6 | 3 |  |  | 446788.086 | -0.037 |
| 9 | 6 | 3 | 8 | 6 | 2 |  |  | 446788.086 | -0.037 |
| 9 | 5 | 5 | 8 | 5 | 4 | 518270.164 | -0.057 | 44E487.780 | 0.014 |
| 9 | 5 | 4 | 8 | 5 | 3 | 518270.164 | -0.057 | 448487.780 | $\leq 0.000$ |
| 9 | 4 | 6 | 8 | 4 | 5 | 520573.366 | 0.016 | 449943.108 | 0.018 |
| 9 | 4 | 5 | 8 | 4 | 4 | 520575.366 | -0.036 | 449945.473 | -0.054 |
| 9 | 3 | 7 | 8 | 3 | 6 | 522340.545 | -0.029 | 431202.148 | 0.112 |
| 9 | 3 | 6 | 8 | 3 | 5 | 522354.373 | -0.024 | 451400.742 | 0.046 |
| 9 | 0 | 9 | 8 | 0 | 8 | 522922736 | 0.061 | . 446028.288 | 0.057 |
| 9 | 2 | 8 | 8 | 2 | 7 | 523158.217 | -0.062 | 450337.485 | 0.039 |
| 9 | 2 | 7 | 8 | 2 | 6 | 524457.508 | 0.047 | 459994.215 | 0.039 |
| 9 | 1 | 8 | 8 | 1 | 7 | 534202.217 | -0.054 | 465187.728 | 0.035 |
| 10 | f | 10 | 9 | 1 | 9 |  |  | 483154.371 | -0.050 |
| 10 | 0 | 10 | 9 | 0 | 9 |  |  | 494131.122 | -0.028 |
| 10 | 6 | 5 | 9 | 6 | 4 |  |  | 496428.850 | 0.046 |
| 10 | 6 | 4 | 9 | 6 | 3 |  |  | 496428.850 | 0.046 |
| 10 | 5 | 6 | 9 | 5 | 5 |  |  | 498331.756 | -0.002 |
| 10 | 5 | 5 | 9 | 5 | 4 |  |  | 498331.756 | -0.040 |
| 10 | 4 | 7 | 9 | 4 | 6 |  |  | 499981.986 | -0.001 |
| 10 | 4 | 6 | 9 | 4 | 5 |  |  | 499987.235 | -0.037 |
| 10 | 2 | 9 | 9 | 2 | 8 |  |  | 500060.590 | -0.028 |
| 10 | 3 | 8 | 9 | 3 | 7 |  |  | 501411.809 | $-0.023$ |
| 10 | 3 | 7 | 9 | 3 | 6 |  |  | 501751.791 | 0.017 |
| 10 | 2 | 8 | 9 | 2 | 7 |  |  | 507709.574 | -0.035 |
| 10 | 1 | 9 | 9 | 1 | 8 |  |  | 516343.92I | -0.076 |

${ }^{*} \mathrm{ln} \mathrm{MHz}$


Figure 1. Spectra of a section of the $J=7-8$ transition of $\mathrm{LiNH}_{2}$ and pari of the $J=8-9$ transition of LiND, near 465 and 451 GHz , respectively. The quantum number labeting is $J_{\text {hax }}$. In the $\mathrm{LiNH}_{2}$ spectrum, the $R_{\mathrm{a}}=0$ and 3 components are present, as well as one component of the $K_{0}=2$ doublet in the inset, the asymmerry splisting of the $K_{e}=3$ component near 464.4 GHz is shown, using an expanided scale. For $\mathrm{LiND}_{2}$, ane line for the $\mathrm{K}_{\mathrm{t}}=2$ doublet is visible but both components for $K_{0}=3$ and 4 arr presens. The effect of suclear spin staristics, coupled with the Boltumann factors, is evident in the dam For $\mathrm{LiNH}_{2}$, the $K_{3}$ odd lines are stroager than the $K_{a}$ evea ones; in the $\mathrm{LiND}_{2}$ spectum, the opposite occurs Both spectre are cramposites of 9 to $16,100 \mathrm{MHiz}$ scans, each lasting approximately 1 min in duration.
$(1+1)(21+1)$, and the para or even $K_{3}$ levels have a degeneracy of $l(21+1)$. This results in ap approximate $3: 1$ intensiry alteration of odd:even $K_{s}$ componems. Thus, the $K_{0}=1$ and 3 components were identified first. These preliminary assigaments were then used to predict the frequencies of additional $\mathcal{K}_{\mathrm{a}}$ components.

For $\mathrm{LiND}_{2}$, nearly 160 CHz of frequency space was initially searched. The final fit of the rotational transitions for $\mathrm{LiND}_{2}$ was obtained by a procedure similar to that described for $\mathrm{LiNH}_{2}$. However, for $\mathrm{LiND}_{2}$, a $\mathrm{C}_{2}$ rotation results in the exchange of the two deuterons, which are bosons ( $I=1$ ), changing the intensity aleration by spin statistics so $2: 1, K_{\mathrm{z}}$ even: $K_{\mathrm{a}}$ odd.

Although the spin statstics observed for borb $\mathrm{LiNH}_{2}$ and $\mathrm{LiND}_{2}$ indicate that they are planar, a pyramidal structure, which undergoes a $C_{2}$ rotation followed by molecular inversion, was also a possible geometric consideration. However, if the molecule were undergoing molecular inversion. an inversion spectram with the opposite spin statisuics of the ground state would be present. In the extensive search for these molecules, an inversion specrum was not observed for either species. Further evidence for a planar geomery is provided by the observation of a small positive inerial defect with limte change on deuterium substitution, which is usually a good indication of planarity. ${ }^{47,48}$ For LiNH ${ }_{2}$, the inertial defect $\Delta=0.115$ amu

Tade 2. Rotational Casstants for LiNH2 and LiND ${ }^{\circ}$

|  | $\underline{\mathrm{La}} \mathrm{NH}_{2}$ | $\mathrm{LiND}_{2}$ |
| :---: | :---: | :---: |
| A | 394567(49) | 197378(3) |
| $\pm$ | 30321.626(20) | 26795.004(23) |
| $C$ | 27978.631(19) | 23428.339(20) |
| $D_{1}$ | 0.149451 (69) | $0.086981(53)$ |
| Dss | 12.9834(29) | $7.9808(20)$ |
| $d_{1}$ | $-0.015485(74)$ | -0.017241(64) |
| $d_{2}$ | -0.007830(42) | -0.01288(10) |
| $H^{\text {m }}$ | -0.01807(26) | -0.003957(94) |
| $\mathrm{H}_{\text {ch }}$ | $0.001003(19)$ | $0.000706(19)$ |
| $\mathrm{b}_{2}$ |  | $1.64(74) \times 10^{-8}$ |
| $\sim_{3}$ | $4.3(2.7) \times 10^{-7}$ | $7.4(1.5) \times 10^{-7}$ |
| $L_{\text {d }}$ | $8.01(82) \times 10^{-6}$ | $1.15(29) \times 10^{-4}$ |
| LxIE | $-3.981(69) \times 10^{-4}$ | $-3.08(16) \times 10^{-5}$ |
| Lusk |  | $-2.02(81) \times 10^{-7}$ |
| ras of fit | 0.045 | 0.040 |

- In MHz; etrors are 3-a and epply to the bast quosed decimal place.
$A^{2}$ and for $\mathrm{LiND}, \Delta=0.150$ amu $A^{2}$. These values are some. what higher bin comparable to those for $\mathrm{NaNH}_{2}$ ( 0.079 amu $\left.A^{2}\right)^{46}$ and for formaldehyde (0.05767 amu $\left.\dot{A}^{2}\right)^{49}$ botb of which are planar. In contrast, for the nonplanar molecules $\mathrm{NH}_{2} \mathrm{OH}$ and $\mathrm{NH}_{2} \mathrm{Cl}$, values of -2.600 gmu $\AA^{2}$ or $-1.032 \AA^{2}$, respectively, have been found. 50.51

Extra lines were observed in the spectra of $\mathrm{LiNH}_{2}$ and $\mathrm{LiND}_{2}$, which may arise from the ${ }^{6} \mathrm{Li}$ isotopomers. However, the ratio of ${ }^{7} \mathrm{Hi}$ and ${ }^{\mathrm{L} \mathrm{L} \mathrm{i} \text { in the natural abundance samples used would be }}$ 12.3 to $1 .{ }^{52}$ Any ${ }^{6} \mathrm{Li}$ lines are therefore over an order of magnitude lower in intensity. While this reduced signal level may not pose a problem for strong $K_{2}=0$ and 1 components, the spectra could not be assigned without observing lines originating in the $K_{\infty}=4$ and 5 levels. Even in more abundan: ${ }^{7} \mathrm{LiNH}_{2}$ and ${ }^{7} \mathrm{LiND}_{2}$, the signals for these components were greatiy reduced relative to the $K_{\mathrm{g}}=0$ and 1 lines. Therefore it Was not surprising that for the corresponding "Li species these simals were not detectable.

Finally, quadrupole interactions due to both the ${ }^{1} \mathrm{Li}(I=3 / 2)$ and the ${ }^{14} \mathrm{~N}(I=1)$ nuclei must be considered, in particular at low $J$. For LiNH 2 , there was no evidence of quadrupole splitting in che $J=1 \rightarrow 2$ transition. The $J=0 \rightarrow 1$ transition, where such splitting is expected to be largest, was not recorded since it was below the attainable frequency range. Failure to observe quadrupole byperfine interactions is not surprising. The dominant nucleus for this splitting should be ${ }^{7} \mathrm{Li}$, since it has a quadrupole moment a factor of 2 larger than that of ${ }^{14} \mathrm{~N} .{ }^{52} \mathrm{On}$ the basis of data for LiH. ${ }^{53}$ the quadrupole coupling constant (eqQ) in $\mathrm{LiNH}_{2}$ is estimated to be less than 350 kHz . Such a value would resadt in a splitting of $<300 \mathrm{kHz}$ in the $J=$ $2-1$ transition, which would not be observable given the line widths of at least about 400 kHz ar the $J=2 \rightarrow 1$ frequency.

For both species, the data were ift with a $A_{1}$ Hamiltonian using the leastosquares fitting program SPFIT. This Hamilonian inchudes miational constants and up so 4th order cenarifugal distortion parameters. For LiNH2, 57 rotational transitions were
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| :--- |
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| species | somrce | $\mathrm{T}_{\mathrm{A}-\mathrm{N}}(\mathrm{A})$ | $n_{N-H}\left(A_{1}\right)$ | On-4-Hif(deg) | ref |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{LiNH}_{2}$ | mm-waye ( $F_{0}$ sincture | 1.736(3) | $1.02243)$ | 106.\%1) | this work |
|  | ab initio (STO-3G) | 1.635 | 1.026 | 102.3 | 56 |
|  | abinicio | 1.782 | $1.01{ }^{\text {c }}$ | 110 | 55 |
|  | ath initio (3-21G bases sel) | 1.714 | 1.013 | 106.5 | 24 |
|  | ab initio (3-21+G basis sel) | 1.759 | 1.013 | 107.0 | 24 |
|  | abinitic (3-21G basis set) | 1.715 | 1.013 | 106.48 | 61 |
|  | 2binitio (4-3I+G beasis set) | 1.754 | 1.005 | 107.58 | 61 |
|  | ab initio (6-31G basis set) | 1.74 | 1.01 | 108 | 24 |
|  | ab initio (6-310 ${ }^{\text {a }}$ basis sely | 1.750 | 1.005 | 105.25 | 61 |
|  | mbinitio (6-310) | 1.740 | 1.016 | 106.5 | 57 |
|  | abinitio (6-31G**) | 1.739 | 1.009 | 10.4 .4 | 57 |
|  | ab initio ( $6-31 \mathrm{C}^{\text {d }}$ ) | 1.750 | 1.005 | 105.2 | 58 |
|  | ab initio (SBK*) | 1.786 | 1.019 | 103.8 | 58 |
|  | mbinitio (TZV*) | 1.728 | 1.002 | 105.2 | 58 |
|  | DMOL-min | 1.697 | 1.134 | 100.8 | 59 |
|  | DMOL-DNP | 1.731 | 1.033 | 104.0 | 59 |
|  | ab initio (MP2/6-311G*) | 1.739 | 1.014 | 105.6 | 59 |
|  | ab inicio (MP2/6-311+G4) | 1.760 | 1.016 | 105.2 | 59 |
|  | ab initio (MIDI-4*) | 1.767 | 1.011 | 103.9 | 62 |
|  | ab inizio (MP2/6-31+ $+\mathrm{G}^{\text {a }}$ ) | 1.754 | nd | nd | 63 |
|  | B3LYP/6-31+ $+\mathrm{G}^{* *}$ | 1.737 | 1.017 | 104.36 | 60 |
|  | B3LYP/6-3i++G** $3 \mathrm{~d} ¢, 2 \mathrm{p}$ ) | 1.732 | 1.015 | 104.27 | 60 |
| $\left(\mathrm{LiNH}_{2}\right)_{2}$ | ab initio ${ }^{\text {a }}$ | 1.869-1.943* | 1.007-1.016 ${ }^{6}$ | 101.7-106 ${ }^{\text {m }}$ | 24 |
| $\left(\mathrm{LiNH}_{2}\right)_{3}$ | ab initios | 1.850-1.95 ${ }^{\circ}$ | 1.017-1.019 ${ }^{\text {d }}$ | 102.3-110 ${ }^{\text {t }}$ | 24 |
| $\left(\mathrm{LiNH}_{2}\right)_{4}$ | $a b$ initio ${ }^{\text {b }}$ | 1.908-2.027 ${ }^{\text {b }}$ | 1.019 | 104.4-105.9 ${ }^{6}$ | 25 |
| (LiNHz) | ab initio ${ }^{\text {b }}$ | 1.844-2.055 ${ }^{\text {a }}$ | 1.018-1.032 ${ }^{\text {a }}$ | $100.6-105.7{ }^{8}$ | 26 |
| $\left(\mathrm{LiNH}_{2}\right)_{5}{ }^{6}$ | X-ray crystallography | 2.059(3), 2.064(9), 2.212(9),2.213(3) | $0.70(10), 0.76(12)$ | nd | 11 |
| $\mathrm{NaNH}_{2}$ | min-wave ( $r_{0}$ structure) | $2.091(3)$ | 1.008(3) | 106.6(1) | 46 and this work |
|  | ah initio (6-316 ${ }^{(1)}$ | 2.080 | 1.007 | 104.4 | 58 |
|  | shinstio (SBK*) | 2.150 | 1.022 | 103.0 | 58 |
|  | ab initio ( $12 \mathrm{~V}^{*}$ ) | 2096 | 1.005 | 104.6 | 58 |
|  | B3LYP/6-31++G** | 2097 | 1.017 | 104.93 | 60 |
|  | B3LYP/6-31++G**(3di.2p) | 2.082 | 1.014 | 104.79 | 60 |
| $\left(\mathrm{NaNH}_{2}\right)_{56^{d}}$ | X-ray crystallography | 2.38-2.50 | nd | nd | 9 |
| $\mathrm{NH}_{2}{ }^{-}$ | infrared spectroscopy |  | 1.041 | 102.1 | 64 |
| $\mathrm{NH}_{2}$ | laser magnetic resonance |  | 1.025 | 103.1 | 65 |

${ }^{\circ}$ Assumed value. ${ }^{b}$ Values depend on geomery assumed and particular basis set employed. 88 molecules in the unil cell. ${ }^{4} 16$ molecules in the unit cell.

## Scheme 2


measured including $K_{\mathrm{a}}$ components up to $K_{\mathrm{a}}=5$, over the frequency range $110-540 \mathrm{GHz}$. For $\mathrm{LiND}_{2}, 60$ rotational transinions were reconded for components as high as $K_{a}=6$. The final constants determined for these species are presented in Table 1 , including the root mean square of the data firs, which indicate an analysis of high precision.
The structure was calculated using a least-squares routine, which determines the bond distances and angles using the moment of inertia equations (e.g. ref 52). The moments of inertia are obtained directly from the measured rorational constants. However, there are three unknowns invoived in the strucnure for $\mathrm{LiNH}_{2}$ and only two such equations, because the molecale is planar. Therefore, two sets of equations were used, one using the moments for $\mathrm{LiNH}_{2}$ and the other those of $\mathrm{LiND}_{2}$, assuming that the bond lengths do not change with isotopic substifution. The least-squares routine obtained the best fit to the stracture using those four equations. Hence, the $\mathrm{r}_{0}$ structure portrayed in Scheme 2 was obtained.
Comparison of Geometrical Parameters with Other Data. First we will discuss the overall geomerry of the $\mathrm{M}-\mathrm{NH}_{2}$ unit.
then we will focus on specific bond leagth and angle data. Although several groups have theoretically predicted a planar structure for $\mathrm{LiNH}_{2}$ (Table 3). the gas-phase data presented here are the first experimental confirmation of this fact and the most direct comparison between experiment and theory. In the previously reperted structures of solid lithium and sodium amide. most attention was paid to the arrangement of amide anions and alkali metal cations in the crystal. As the data in Table 3 indicate, the lithium and sodium congeners contain 8 and 16 molecules, respectively, in their unit cells. Significantly, whereas our data show that both monomeric LiNH $\mathrm{Lin}_{2}$ and $\mathrm{NaNH}_{2}$ are planar, the crystal packing of solid samples of these species made it impossible to say whetber individual $\mathrm{MNH}_{2}$ units were planar or tetrahedral. ${ }^{9.11}$ Only in the structure of solid LiNH2 was it possible to identify the positions of the $H$ atoms. ${ }^{11}$ However, in the best reported crystal structure of $\mathrm{LiNH}_{2}$ relazively large standard deviations in H-atom positions precludes meaningful comparison of $\mathrm{N}-\mathrm{H}$ bond length and $\mathrm{H}-\mathrm{N}-\mathrm{H}$ angle with our gras-phase data. In addition, the fundamental difficulty with crystal data is that the orientation of each of the eight amide anions in the unit cell of $\mathrm{LiNH}_{2}$ clearly varies, precluding any conclusion about the geometry of a hypothetical $\mathrm{LiNH}_{2}$ monomeric unit in the crystal. Only in later structures of monomeric, solvated $\mathrm{M}-\mathrm{NR}_{2}$ or $\mathrm{M}-\mathrm{NHR}$ (for examples, see Scheme 1) was it possible to see that the $M-\mathrm{NR}_{2}$ unit was planar, but in shese samples the $\mathbb{R}$ groups are very large or contain groups capable of delocalizing negative charge, features expected to encourage planarity. The $\mathrm{Li}-\mathrm{N}$ bond distance in LiNH2 is 0.16 A shoner than that in 1 (Scheme
1). which to our knowledge is the jithium amide featuring the shorest $\mathrm{Li}-\mathrm{N}$ boad to date. This difference underscores the combined effects of solvation and large nitrogen substuruents in increasing the bood distance. The observed $\mathrm{M}-\mathrm{N}$ distance in $\mathrm{NaNH}_{2}{ }^{4 \mathrm{O}}$ is longer than that in LiNH2, as expected. The $\mathrm{H}-\mathrm{N}-\mathrm{H}$ angle in $\mathrm{NaNH} \mathrm{H}_{2}$ is $106.6^{\circ}$. based on sew data obtained by Sheridan and Ziurys for $\mathrm{NaND}_{2}$ (see Supporting Information). Therefore, this angle is almost identical to that in $\mathrm{LiNH}_{2}$ $\left[106.9(1)^{c}\right]$, a result in complete agreement with the relatively constan $\mathrm{H}-\mathrm{C}-\mathrm{H}$ angle in $\left.\mathrm{M}-\mathrm{CH}_{3}(\mathrm{M}=\mathrm{Li}, \mathrm{Na}, \mathrm{K})\right)^{54}$
Approximately 20 calculated strictures for $\mathrm{LiNH}_{2}$ monomer have been reported in the literature, yet our data provide the first direct experimental test. From Table 3 it appears that earlier lower level calculations ${ }^{55,56}$ gave the poorest results, whereas higher level ab initio calculations with 6.31 G or larger basis sels provide the best structures. ${ }^{25,57-60}$ Of note is a recent
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coraparison of these methods with DFI calculations, which can also give good geometries as shown by results with DMOL-DNP. ${ }^{39}$

## Comelusions

The simplest lithium amide, $\mathrm{LiNH}_{2}$, serves as a model for larger amides used in symthesis and structural strudies. Its structure has been predicted several times in the literature. without direct experimental evidence for comparison until now. Here, gas-phase synthesis led to formation of the unsolvated monomer LiNH $\mathrm{L}_{2}$ and microwave spectroscopy allowed its precise structure to be determined. The data here verify prediction of its planarity, showing in addition that higher level alb initio and DFT calculations provide accurate stuctural information. The resulss show the usefulness of gas-phase data on low-ccordinate organometallic complexes, which will be the subjeci of furtber reporis.

Achnewledgunent. This research was supported by National Science Foundation grant CHE 9531244 (to D.B.G. and L.M.Z.) and NASA grant NAG $5-3785$ (to L.M.Z.).

Supporting Informatiem Available: Observed transitions for $\mathrm{NaND}_{2}$ (PDF). This material is available free of charge via the loternet at httip:/pubs.acs.org.
JA003422 H

[^5]Table S1. Measured Rotational Transition Frequencies for $\mathrm{NaND}_{2}\left(\mathrm{X}^{1} \mathrm{~A}_{1}\right)^{\text {a) }}$

| J |  | $\mathrm{K}_{\mathrm{c}}{ }^{\prime}$ | $\leftarrow \mathrm{J}^{19}$ |  | $\mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ | $\psi_{\text {obs }}$ | $\nu_{\text {obs }} \cdot \nu_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 15 | 2 | 13 | 14 | 2 | 12 | 289070.049 | -0.043 |
| 15 | 1 | 14 | 14 | 1 | 13 | 292310.754 | -0.068 |
| 17 | 1 | 17 | 16 | 1 | 16 | 322788.135 | -0.048 |
| 17 | 6 | 12 | 16 | 6 | 11 | 325372.643 | -0.005 |
| 17 | 6 | 11 | 16 | 6 | 10 | 325372.643 | -0.005 |
| 17 | 5 | 13 | 16 | 5 | 12 | 325972.676 | 0.050 |
| 17 | 5 | 12 | 16 | 5 | 11 | 325972.676 | 0.050 |
| 17 | 0 | 17 | 16 | 0 | 16 | 326424.626 | -0.044 |
| 17 | 4 | 14 | 16 | 4 | 13 | 326462.895 | 0.064 |
| 17 | 4 | 13 | 16 | 4 | 12 | 326462.895 | -0.023 |
| 17 | 2 | 16 | 16 | 2 | 15 | 326898.348 | -0.087 |
| 17 | 2 | 15 | 16 | 2 | 14 | 327686.617 | -0.100 |
| 17 | 1 | 16 | 16 | 1 | 15 | 331162.920 | -0.027 |
| 18 | 1 | 18 | 17 | 1 | 17 | 341712.991 | -0.025 |
| 18 | 6 | 13 | 17 | 6 | 12 | 344477.342 | 0.008 |
| 18 | 6 | 12 | 17 | 6 | 11 | 344477.342 | 0.008 |
| 18 | 5 | 14 | 17 | 5 | 13 | 345112.949 | 0.001 |
| 18 | 5 | 13 | 17 | 5 | 12 | 345112.949 | $<0.000$ |
| 18 | 0 | 18 | 17 | 0 | 17 | 345484.107 | 0.002 |
| 18 | 4 | 15 | 17 | 4 | 14 | 345633.808 | 0.087 |
| 18 | 4 | 14 | 17 | 4 | 13 | 345633.808 | -0.043 |
| 18 | 3 | 16 | 17 | 3 | 15 | 346062.305 | -0.025 |
| 18 | 2 | 17 | 17 | 2 | 16 | 346070.521 | -0.027 |
| 18 | 3 | 15 | 17 | 3 | 14 | 346080.318 | -0.044 |
| 18 | 2 | 16 | 17 | 2 | 15 | 347004.297 | -0.026 |
| 18 | 1 | 17 | 17 | 1 | 16 | 350571.807 | -0.016 |
| 19 | 1 | 19 | 18 | 1 | 18 | 360627.353 | -0.004 |
| 19 | 6 | 14 | 18 | 6 | 13 | 363576.038 | 0.024 |
| 19 | 6 | 13 | 18 | 6 | 12 | 363576.038 | 0.024 |
| 19 | 5 | 15 | 18 | 5 | 14 | 364247.302 | -0.028 |
| 19 | 5 | 14 | 18 | 5 | 13 | 364247.302 | -0.023 |
| 19 | 0 | 19 | 18 | 0 | 18 | 364520.059 | 0.025 |
| 19 | 4 | 16 | 18 | 4 | 15 | 364799.083 | 0.116 |
| 19 | 4 | 15 | 18 | 4 | 14 | 364799.083 | -0.074 |
| 19 | 3 | 17 | 18 | 3 | 16 | 365255.218 | 0.059 |
| 19 | 3 | 16 | 18 | 3 | 15 | 365278.787 | -0.023 |
| 19 | 2 | 18 | 18 | 2 | 17 | 365232.866 | -0.003 |
| 19 | 2 | 17 | 18 | 2 | 16 | 366328.295 | 0.007 |
| 19 | 1 | 18 | 18 | 1 | 17 | 369968.275 | 0.024 |
| 20 | 1 | 20 | 19 | 1 | 19 | 379530.707 | 0.016 |
| 20 | 6 | 15 | 19 | 6 | 14 | 382668.355 | 0.008 |
| 20 | 6 | 14 | 19 | 6 | 13 | 382668.355 | 0.008 |

Table S1. Cont'd.

| $\mathrm{J}^{\prime} \mathrm{K}_{\mathrm{a}}{ }^{+} \mathrm{K}_{\mathrm{c}}{ }^{\text {c }} \leftarrow \mathrm{J}^{\prime \prime} \mathrm{K}_{\mathrm{a}}{ }^{\prime \prime} \mathrm{K}_{\mathrm{c}}{ }^{\prime \prime}$ |  |  |  |  |  | $\nu_{\text {obs }}$ | $\nu_{\text {obs }-} v_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 20 | 5 | 16 | 19 |  | 15 | 383375.410 | -0.026 |
| 20 | 5 | 15 | 19 | 5 | 14 | 383375.410 | -0.027 |
| 20 | 4 | 17 | 19 | 4 | 16 | 383958.404 | 0.157 |
| 20 | 4 | 16 | 19 | 4 | 15 | 383958.404 | -0.116 |
| 20 | 3 | 18 | 19 | 3 | 17 | 384442.421 | 0.055 |
| 20 | 3 | 17 | 19 | 3 | 16 | 384472.962 | 0.010 |
| 20 | 2 | 19 | 19 | 2 | 18 | 384384.857 | $<0.000$ |
| 20 | 2 | 18 | 19 | 2 | 17 | 385658.673 | 0.025 |
| 20 | 1 | 19 | 19 |  | 18 | 389351.528 | 0.051 |
| 21 | 1 | 21 | 20 | 1 | 20 | 398422.559 | 0.042 |
| 21 | 6 | 16 | 20 | 6 | 15 | 401753.975 | -0.018 |
| 21 | 6 | 15 | 20 | 6 | 14 | 401753.975 | -0.018 |
| 21 | 5 | 17 | 20 | 5 | 16 | 402496.851 | -0.079 |
| 21 | 5 | 16 | 20 | 5 | 15 | 402496.851 | -0.081 |
| 21 | 0 | 21 | 20 | 0 | 20 | 402517.589 | 0.087 |
| 21 | 4 | 18 | 20 | 4 | 17 | 403111.411 | 0.171 |
| 21 | 4 | 17 | 20 | 4 | 16 | 403111.411 | -0.216 |
| 21 | 3 | 18 | 20 | 3 | 17 | 403662.662 | 0.031 |
| 21 | 2 | 20 | 20 | 2 | 19 | 403526.013 | 0.038 |
| 21 | 2 | 19 | 20 | 2 | 18 | 404995.414 | 0.052 |
| 21 | 1 | 20 | 20 | 1 | 19 | 408720.814 | 0.077 |
| 27 | 1 | 27 | 26 | 1 | 26 | 511505.068 | 0.030 |
| 27 | 0 | 27 | 26 | 0 | 26 | 515861.700 | 0.055 |
| 27 |  | 24 | 26 | 4 | 23 | 517879.283 | 0.304 |
| 27 | 4 | 23 | 26 | 4 | 22 | 517880.972 | -0.274 |
| 27 | 3 | 25 | 26 | 3 | 24 | 518562.876 | 0.011 |
| 27 | 3 | 24 | 26 | 3 | 23 | 518699.834 | 0.123 |
| 27 | 2 | 26 | 26 | 2 | 25 | 518114.474 | 0.056 |
| 27 | 2 | 25 | 26 | 2 | 24 | 521134.489 | 0.016 |
| 27 |  | 26 | 26 | 1 | 25 | 524598.873 | 0.015 |
| 28 | 1 | 28 | 27 | 1 | 27 | 530303.113 | -0.061 |
| 28 | 6 | 23 | 27 | 6 | 22 | 535137.239 | -0.017 |
| 28 | 6 | 22 | 27 | 6 | 21 | 535137.239 | -0.017 |
| 28 | 5 | 24 | 27 |  | 23 | 536133.889 | 0.126 |
| 28 | 5 | 23 | 27 | 5 | 22 | 536133.889 | 0.099 |
| 28 |  | 28 | 27 | 0 | 27 | 534652.812 | -0.055 |
| 28 |  | 25 | 27 | 4 | 24 | 536978.853 | 0.028 |
| 28 | 4 | 24 | 27 | 4 | 23 | 536981.539 | -0.213 |
| 28 |  | 26 | 27 | 3 | 25 | 537690.795 | -0.022 |
| 28 | 3 | 25 | 27 |  | 24 | 537854.739 | -0.021 |
| 28 | 2 | 27 | 27 | 2 | 26 | 537164.464 | -0.018 |
| 28 | 2 | 26 | 27 | 2 | 25 | 540506.042 | -0.007 |
| 28 | 1 | 27 | 27 | 1 | 26 | 543847.941 | -0.098 |

a) In MHz.

Table S2. Spectroscopic Constants for $\mathrm{NaND}_{2}\left(\mathrm{X}^{1} \mathrm{~A}_{1}\right)$

| Constant | $\mathrm{NaND}_{2}(\mathrm{MHz})$ |
| :---: | :---: |
| A | $195058(8)$ |
| B | $9881.5860(58)$ |
| C | $9385.9150(52)$ |
| $\mathrm{D}_{\mathrm{J}}$ | $0.0163322(24)$ |
| $\mathrm{D}_{\mathrm{JK}}$ | $1.151691(88)$ |
| $\mathrm{d}_{1}$ | $-0.0009734(22)$ |
| $\mathrm{d}_{2}$ | $-0.0003490(35)$ |
| $\mathrm{H}_{\mathrm{JK}}$ | $0.0000370(13)$ |
| $\mathrm{H}_{\mathrm{KJ}}$ | $-0.000726(40)$ |
| $\mathrm{h}_{2}$ | $1.34(33) \times 10^{-8}$ |
| $\mathrm{~h}_{3}$ | $4.21(78) \times 10^{-9}$ |
| $\mathrm{~L}_{\mathrm{KK}}$ | $1.02(63) \times 10^{-7}$ |
| $\mathrm{~L}_{\mathrm{JJK}}$ | $-2.02(55) \times 10^{-9}$ |
| $\mathrm{P}_{\mathrm{KJ}}$ | $-3.10(18) \times 10^{-7}$ |
| $\mathrm{P}_{\mathrm{JK}}$ | $-1.7(1.1) \times 10^{-9}$ |
| rms of fit | 0.071 |

## APPENDIXE

THE PURE ROTATIONAL SPECTRUM OF NaC IN ITS X ${ }^{4} \Sigma$ n STATE: OBSERVATION AND INTERPRETATION
P. M. Sheridan, L. M. Ziurys, S. A. Beaton, S. M. Kermode, and J. M. Brown, J. Chem. Phys. 116, 5544-5550 (2002).

# The pure rotational spectrum of NaC in its $X^{4} 5^{-}$state: Observation and interpretation 

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## 1. INTRODUCTION

There are several reasons for the recent interest in the study of the metal monocarbides. Amongst these are the need to know more about the metal-carbon bond. ${ }^{1}$ its relevance to organic reagents ${ }^{2}$ and catalytic processes. ${ }^{3}$ the presence of such compounds in the circumstellar envelope of late-type stars. ${ }^{4}$ and the possible use of these compounds as high energy density fuels. ${ }^{\text {² }}$ An increasing amount of information on metal carbides is now available from electronic spectroscopy ${ }^{5-15}$ and more recently, from rotational spectroscopy. ${ }^{16.17}$ The species are generated by a variety of experimental techniques. including the use of high temperature ovens or by laser ablation methods in the presence of a suitable precursor.

In a recent paper. ${ }^{17}$ we reported the first detection of the KC radical in its $X^{4}{ }^{-}$- state by millimeter-wave spectroscopy. The molecule was formed using a Broida oven as a source of polassium vapor, which was then reacted with $\mathrm{CH}_{4}$. The measurements of rotational transition frequencies between 344 and 515 GHz were used to determine the parameters of an effective Hamilionian for a molecule in a ${ }^{+5}$ state. The present paper reporss an analogous study of the NaC free radical. This species is of particular interest because other sodium-containing molecules have been detected in carbon-rich stars. ${ }^{18.19}$ It is also informative to compare the metal-carbon bond in NaC with that in NaCH and $\mathrm{NaCH}_{3} \cdot{ }^{20.21}$ In the course of the data analysis, an ambiguity in the fituing procedure was discovered. Two equally good

[^6]fits were obtained but with different values for the parameters, particularly the spin-spin parameter $\lambda$. The reasons for preferring one fit to the other have been investigated: a theoretical estimate of the value for $\lambda$ points io a stronger preference for the fit with the smaller $\lambda$-value. The same ambiguity arises for the treament of the carlier spectal data for KC. ${ }^{17}$ Consequently, a reanalysis of the tit is required. These results are also reported in this paper.

## H. EXPERIMENT

The pure rotational spectrum of NaC was recorded using one of the quasi-optical millimeter-wave spectrometers of the Ziurys group (see Ref. 22). Phase-iocked Gunn oscillators and Schouky diode multipliers are used in combination to produce radiation in the $65-540 \mathrm{GHz}$ range. The millimeter-waves are launched from a scalar feedhom and passed through a polarizing grid. Tetion lenses are used to collimate the radiation through the double pass reaction cell. a 0.5 m long steel vacuum charber. A roofiop rellector is located at the rear of the cell. which rotates the polarization of the incident radiation by $90^{\circ}$. The radiation is directed. after the second pass through the cell. into an $\operatorname{lnSb}$ bolometer cooled to liquid helium temperatures. The signal is frequency-modulated at 25 kHz and recorded as a second derivative spectrum using a lock-in amplifier.

VaC was synthesized from the reaction of sodium vapor with methane gas in a de discharge. The sodium vapor was created by using a Broda-lype oven atached to the reaction chamber. Approximately $20-30 \mathrm{mTorr}$ of methane and $10-15 \mathrm{~m}$ Jorr of argon were fowed into the reaction chamber from underneath the oven. thus entraining the metal vapor. A


FIG. 1. A spectrum of the $N=18-17$ rotational transition of NaC . The fine stucture due to the 'E' ground electronic state is clearly visible. The middle componeng hass a higher intensity because it is composed of the $J$ $=17.5-16.5$ and $J=18.5-17.5$ fine stracsure lines which are nestly col lopsed in frequency. This effect resulis in a pseudo-cipiet strucuare. The specturn represens one scan. 60 Minz in with and approximstely imin un duration.
de discharge was then applied to this gas mixture using an electrode located 5 cm above the oven. A current of 0.5-0.7 A at a voltage of 200 V were the optimal discharge conditions: however, it was also found that a lower current of 0.02 A at 200 V also produced the radical. The NaCH radical, and to a lesser extent $\mathrm{NaCH}_{3}$, were produced under the same conditions.

Final measurements of the rotational lines were made by taking an even number of 5 MHz scans. alternately increasing and decreasing in frequency. Up to 32 such scans were required for data measured below 300 GHz . Each line profile was fit with a Gaussian curve to establish the center frequency. Linewidths ranged from 600 to 1500 kHz with an experimental accuracy estimated at $\pm 100 \mathrm{kHz}$.

## III. RESULTS

Limited theoretical investigations of the alkali carbides have predicted that these species possess a ${ }^{+} \Sigma^{-}$ground clectronic state. ${ }^{3-25}$ Our recent high-resolution study of KC (Ref. 17) confirmed the results of these theoretical treatments, as indicated by the distinct quartet structure observed in the millimener-wave spectrum of this radical. In order to probe eiectronic structure of the ligher alkali carbides further, sodium metal was reacted with methane. under conditions similar to those which produced KC. in the hope of producing NaC . An intensive search in frequency space lover a range of about 25 GHz ) for the products of the above reaction, however. yielded a repeating triplet feature, which was found to be unrelated to $\mathrm{NaCH}\left(X^{3} \Sigma^{-}\right) .^{31}$ Closer inspection of the middle component of this set showed that the intensity of this line was approximately twice that of the outer two features. Figure 1 shows this characteristic pattem. which was determined to be the $N=18-17$ totational transition of NaC . It can be seen that the $J=17.5-16.5$ and $J$


FIG. 2. The spectum of NaC obrained at tower frequency: the $N=11$ - 10 mansition is shown. Again. fine structure splinings are present. The middle feature. however. has an unusually broad finewidth which can be decomposed inso two separate compronents corresponding to the $J=10.5$ - 9.5 and $J=11.5-10.5$ fine struchure lines. This spectrum was obasined by averaging 32 scans. esch 12 MHz in width and 1 min in duration.
$=18.5-17.5$ ine structure components are collapsed into a single unresolvable line. In the measurements of subsequent rotational uransitions. these two middle fine structure components could not be resolved. At lower frequencies. these blended components began to split apar such that iwo Gaussian-type curves could be fit to the line profile. This effect is illustrated in Fig. 2, which shows the $\hat{V}=11-10$ wansition of NaC . The brnadening of this line suggests that the two middle fine structure components could be fully resolved at even lower $N$. Atempts to measure the transitions at frequencies lower than 231 GHz in order to observe the completely resolved fine structure proved unsuccessful duc to the transient nature of VaC .

In addition to the fine structurc, a jurther spliting of the lines is expected if hypertine interactions due to the nuelear spin of the sodium atom. $l=3 / 2$. are significant. No hyperfine spliting was observed. consistent with the idea that the umpaired electrons are localized primarily on the carbon atom.

The measured rotational frequencies of VaC are given in Table I. In total. thintem transitions, cach consisting of four fine structure components (nol always resolved). were recorded. The two central components are sotally blended for most of the transitions observed. Only al lower $A$ was this feature deconvolved into two separate lines. albeit the components are still somewhat overtapped.

## M. DETERMination of molecular parameters FOR A ${ }^{5}$ S STATE

## A. The effective Hamilfonian

The observed transition frequencies of NaC were modeled by the following effective Hamiltonian. which was found to be adequate to fit the very accurate rotational data:

$$
\begin{equation*}
H_{\mathrm{en}}=H_{\mathrm{tu}}+H_{\mathrm{vd}}+H_{\mathrm{ss}}+H_{\mathrm{sr}}+H_{\mathrm{u}}^{3} . \tag{111}
\end{equation*}
$$

TABLE I Mcasured motational mansition frequencies for $\mathrm{NaC}\left(\mathrm{N}^{-4} \mathrm{E}^{-1}{ }^{1}\right.$

| $N^{*}$ | $J^{\prime}$ | $\lambda^{*}$ | $J$ | $w_{0 \times 5}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 9 | 7.5 | 8 | 6.5 | 231391.590 | -0.161 |
| 9 | 8.5 | 8 | 7.5 | 231395.612 | -0.294 |
| 9 | 9.5 | 8 | 8.5 | 291394.132 | - 0.186 |
| 9 | 10.5 | 8 | 9.5 | 231398.113 | -0.063 |
| 10 | 8.5 | 9 | 7.5 | 257065.258 | 0.227 |
| 10 | 9.5 | 9. | 8.5 | 257059.032 | -0.171 |
| 10 | 10.5 | 9 | 9.5 | 237067.962 | -0.146 |
| 10 | 11.5 | 9 | 10.5 | 257071.942 | -0.007 |
| 11 | 9.5 | 10 | 8.5 | 282726.850 | 0.106 |
| 11 | 10.5 | 10 | 9.5 | 282731.046 | 0.113 |
| 11 | 11.5 | 10 | 10.5 | 282730.280 | 0.081 |
| 11 | 12.5 | 10 | 11.5 | 282734.087 | 0.064 |
| 12 | 10.5 | 11 | 9.5 | 308375.816 | 0.123 |
| 12 | 11.5 | 11 | 10.5 | 308380.042 | 0.143 |
| 12 | 12.5 | 11 | 11.5 | 308379.448 | 0.012 |
| 12 | 13.5 | 11 | 12.5 | 308383.293 | 0.048 |
| 13 | 18.5 | 12 | 10.5 | 334010.762 | 0.068 |
| 13 | 12.5 | 12 | 11.5 | 334014.769 | -0.011 |
| 13 | 13.5 | 12 | 12.5 | 334014.769 | 0.018 |
| 13 | 14.5 | 12 | 13.5 | 338018.450 | -0.00s |
| 14 | 12.5 | 13 | 11.5 | 359630.610 | 0.042 |
| 14 | 13.5 | 13 | 15.5 | 359634.508 | -0.247 |
| 14 | 14.5 | 13 | 13.5 | 359634.508 | -0255 |
| 14 | 15.5 | 13 | 14.5 | 359638.489 | -0.003 |
| 15 | 13.5 | 14 | 12.5 | 385234.150 | 0.099 |
| 15 | 14.5 | 14 | 13.5 | 385238.527 | 0.050 |
| 15 | 15.5 | 14 | 14.5 | 38.5238 .527 | 0.167 |
| 15 | 16.5 | 14 | 15.5 | 385242.235 | 0.026 |
| 16 | 14.5 | 15 | 13.5 | 410820.261 | -0.019 |
| 16 | 15.5 | 15 | 14.5 | $410 \$ 24.690$ | 0.101 |
| 16 | 16.5 | 15 | 15.5 | \$10824.690 | 0.094 |
| 16 | 17.5 | 15 | 18.5 | 410828.374 | -0.035 |
| 17 | 15.5 | 16 | 14.5 | 436387.729 | 0.028 |
| 17 | 16.5 | 16 | 15.5 | 436392.177 | 0.068 |
| 17 | 17.5 | 16 | 16.5 | 436.392 .177 | 0.061 |
| 17 | 18.5 | 16 | 17.5 | 436395.937 | -0.020 |
| 18 | 16.5 | 17 | 15.5 | 461935.271 | -0.079 |
| 18 | 17.9 | 17 | 16.5 | 461939.880 | 0.064 |
| 18 | 18.5 | 17 | 17.5 | 461939.880 | 0.057 |
| 18 | 19.5 | 17 | 18.5 | 461943.685 | 0.004 |
| 19 | 17.5 | 18 | 16.5 | 487861.934 | -0.088 |
| 19 | 18.5 | 18 | 17.5 | 487466.570 | 0.034 |
| 19 | 19.5 | 18 | 18.5 | $487865.5 \%$ | 0.027 |
| 19 | 20.5 | 18 | 19.5 | 487470.432 | 0.016 |
| 20 | 18.5 | 19 | 17.5 | 512966.432 | -0.116 |
| 20 | 19.5 | 89 | 18.5 | 512971.121 | 0.014 |
| 20 | 20.5 | 19 | 19.5 | 512971.121 | 0.006 |
| 20 | 21.5 | 19 | 20.5 | 512975.018 | 0.022 |
| 21 | 19.5 | 20 | 18.5 | 538447.665 | -0.097 |
| 21 | 20.5 | 20 | 19.5 | 538452.413 | 0.049 |
| 21 | 21.5 | . 20 | 20.5 | 538452.413 | -0.04? |
| 21 | 22.5 | 20 | 21.5 | 598486.295 | 0.038 . |

$$
\begin{align*}
& \text { where } \\
& \qquad \begin{aligned}
H_{\mathrm{rog}} & =B \mathrm{~N}^{2}, \\
H_{\mathrm{cd}} & =-D\left(\mathrm{~N}^{2}\right)^{2}+H\left(\mathbb{N}^{2}\right)^{3}, \\
H_{\mathrm{ss}} & =(2 / 3) \lambda\left(3 S_{:}^{2}-S^{2}\right)+(2 / 3) \lambda_{D}\left(3 S_{:}^{2}-S^{2}\right) \mathrm{N}^{2}, \\
H_{\mathrm{st}} & =\gamma(\mathrm{N} \cdot \mathrm{~S})+\gamma_{D}(\mathrm{~N} \cdot \mathrm{~S}) \mathrm{N}^{2},
\end{aligned} \tag{2}
\end{align*}
$$

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$$
\begin{equation*}
\left.H_{\mathrm{sr}}^{(3)}=(10 / \sqrt{6}) \gamma_{S^{3}} \mathrm{~T}^{3} \mathrm{~L}^{2}, \mathrm{~N}\right) \cdot T^{3}(S . S . S) . \tag{6}
\end{equation*}
$$

The conriburions in Eqs. (2)-(5) inclusive are the familiar zerms involving the rotational kinetic energy, the spinspin dipolar coupling, the spin-rotation interaction, and the centrifugal distortion correction terms. ${ }^{26}$ The term in Eq. (6) is the higher-arder spin-rotation interaction expressed in spherical tensor notation. ${ }^{27}$ It only arises for molecules in states of quarter or higher multiplicity.

When the Hamilonian in Eq. (1) was fitted to the experimental data for NaC , two different bus essentially equivalent solutions to the least-squares problem were discovered. The iwo fits were of the same quality as measured by the standard deviation of the fit but the parameters obtained, particularly the spin-spin parameter $\lambda$, had different values.
B. Origin of the ambiguity in the fit of the rotational spectrum of a molacule in a ${ }^{4} 5$ state

In order to appreciate how the ambiguity of the ${ }^{75}$ rotational energy level scheme arises. let us consider a simplified version of the effective Hamitonian containing the rotational kinetic energy, the spin-spin coupling, and the spin-rotation interaction only, from Eqs. (2), (4), and (5). The energy level scheme for NaC conforms reasonably closely to Hund's case (b) coupling. In this situation, the energies of the four spin components for each rotational level $N(>1)$ are given by

$$
\begin{align*}
F_{1}: F(N)= & B N(N+1)-2 \lambda N /(2 N+3)-12 \lambda^{2}(N+1) \\
& \times(N+3) /\left[2 B(2 N+3)^{3}\right]+3 \gamma N / 2  \tag{7}\\
F_{2}: F(N)= & B N(N+1)+2 \lambda(N+3) /(2 N+3) \\
& -\left(2 \lambda^{2} N(N+2) /\left[2 B(2 N+3)^{3}\right]\right. \\
& +\gamma(N-3) / 2  \tag{8}\\
F_{3}: F(N)= & B N(N+1)+2 \lambda(N-2) / 12 N-1) \\
& +\left(2 \lambda^{2}(N-1)(N+1) /\left(2 B(2 N-1)^{3}\right]\right. \\
& -\gamma(N+4) / 2  \tag{9}\\
F_{4}: F(N)= & B N(N+1)-2 \lambda(N+1) /(2 N-1) \\
& +12 \lambda^{2} N(N-2) /\left[2 B(2 N-1)^{3}\right] \\
& -3 \gamma(N+1) / 2 \tag{10}
\end{align*}
$$

where, as usual, $J=N+\frac{1}{2}$ for the $F_{1}$ component, $J=N+\frac{1}{2}$ for the $F_{2}$ component, and so on. These expressions are derived from the matrix elements in a Hund's case (b) basis set given, for example, by Cheung. Hanson, and Merer: ${ }^{28}$ the effects of the matrix elements off-diagonal in $N$ by 2 have been treated by second order perturbation theory. The contributions involving the spin-spin parameter $\lambda$ can be rearranged to give the following simplified expressions.

$$
\begin{align*}
F_{1}: F(N)= & B N(N+1)-\lambda-3\left[(\lambda-B)^{2}-B^{2}\right] / \\
& {[2 B(2 N+3)]+3 \gamma N / 2 }  \tag{11}\\
F_{2}: F(N)= & B N(N+1)+\lambda-3\left[(\lambda-B)^{2}-B^{2}\right] /
\end{align*}
$$

$$
\begin{equation*}
[2 B(2 N+3)]+\gamma(N-3) / 2 \tag{12}
\end{equation*}
$$

TABLE II. Calculated transifion freameacies and line suengins of the ane suructure coraponems of the $N=18-17$ fonationad tramsition of NaC in its $\operatorname{six}^{\text {S }}$ - state.

| $\begin{gathered} N=18-17 \\ J \end{gathered}$ | $\lambda=64.6 \mathrm{MfH}$ |  | $\lambda=25667.4 \mathrm{MHz}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $8^{\text {B }}$ | Linse swengh | $v^{*}$ | Line strengah |
| 19.5-18.5 | 461 943.7 | 19.46 | \$61 443.6 | 19.46 |
| 18.5-17.5 | 461980.0 | 18.40 | 461939.9 | 18.41 |
| 17.5-16.5 | 461939.7 | 17.80 | 461939.8 | 17.40 |
| 16.5-15.5 | 461935.3 | 16.46 | 461935.3 | 16.45 |
| 18.5-18.5 | 462000.7 | $0.83 \times 10^{-1}$ | 513202.3 | $0.75 \times 10^{-1}$ |
| 17.5-17.4 | 461912.2 | 0.11 | 461920.2 | 0.11 |
| 16.5-16.5 | 2361734.4 | $0.83 \times 10^{-1}$ | - 10538.4 | $0.94 \times 10^{-1}$ |
| 17.5-18.5 | 461972.9 | $0.12 \times 10^{-3}$ | 513182.6 | $0.25 \times 10^{-8}$ |
| 16.5-17.5 | 461706.9 | $0.13 \times 10^{-3}$ | \$10508.8 | $0.32 \times 10^{-8}$ |

${ }^{4}$ Values in MHz

$$
\begin{gather*}
F_{3}: F(N)=B N(N+1)+\lambda+3\left[(\lambda-B)^{2}-B^{2}\right] \\
 \tag{13}\\
\left.F_{4}: F(N)=B N(2 N-1)\right]-\gamma(N+4) / 2 \\
 \tag{14}\\
\\
{[2 B(2 N-1)]-3 \gamma(N+1) / 2 .}
\end{gather*}
$$

These expressions neglect small terns of the order of $\lambda^{2} / 4 B N^{2}$. The transitions detected in NaC all obey the selection rule $\Delta J=\Delta N$ since these are much the strongest for the intermediate $N$ values observed. For this type of transition, the constant term $\pm \lambda$ in the energy level expressions cancels out when the difference in the energies is computed. The transition frequencies thus depend only weakly on the spinspin parameier $\lambda$ through the third term in Eqs. (11)-(14) which is inversely proportional to $N$. The coefficient of this contribution, which is what is deternined in the least-squares fit of the data, depends on the quantity $(\lambda-B)^{2}$. We can thus see that there are two solutions to the modeling problem, depending on whether $(\lambda-B)$ is positive or negative. Since the rotational constant $B$, which must be positive. is determined from the coefficient of $N(N+1)$ in Eqs. (111-(14), the burden of the sign ambiguity is transferred to the parameter $\lambda$. Other aspects of the ambiguities in the determination of the parameters for a molecule in a "E' state are discussed in the Appendix.

The ambiguous nature of the solution to the fiting problem for molecules in ${ }^{+5}$ states which follow Hund 's case (b) coupling could be resolved by detection of the satellite lines with $\triangle J \neq A N$. These lines are separated from the main lines by an amount on the order of $A$ [see Eqs. (11)-(141]. However they will be very much weaker. In Table II. we repor the calculated transition frequencies and line strengets for the fine structure transitions associsted with the rotational transition $N=18-17$ of NaC in its $X^{+5}{ }^{-}$state. Attempts were made to derect the $\Delta J=0$ transitions experimentally at these predicted frequencies but withour success. Since they are expected to be more than two orders of magnitude weaker than the main lines. this is not altogether surprising.

## C. Results of the least-square fits

The measuremens and assignments of rotational transitions in NaC given in Table I were used to determine the parameters of the effective Hamihonian given in Eq. (1). Each measurement was weighted as the inverse square of the estimated experimental uncernainty ( 100 kHz ). For those transitions with $N$ greater than 12. for which the two central components, $F_{2}$ and $F_{3}$, are not resolved, the observed feature was firted to the average of the two calculated transition frequencies. There are 43 independent measurements incladed in the fit. The sextic centrifugal distorion parameter $H$ in Eq. (3) was not deternined significantly in the fits and was therefore constrained to zero. The fit converged to two separate minima of roughly the same guality. The results of the two fits are given in Table III, where the two sets of parameters are listed. Fit A gives a small value for $\lambda$ and fit B a large value. The standard deviations for these fits relative to the estimated experimental uncenainty are 1.017 for fit A and 1.056 for fit $B$, that is nearly the same though slightly better for fit A. The residuals obtained for tit $A$ are listed with the freguencies in Table I: for the reasons given in the Discussion, we believe this to be the correct solution to the fiting problem. The patern of residuals for fit $B$ is broadly similar.

TABLE III. Values for the rotational and fine-structure paraneers determined for NaC in the $0=0$ kevel of its $\mathrm{A}^{-4} \mathrm{~S}^{-}$shate.

| Parameter | Fit A . |  | Fin $B$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | Value ${ }^{2}$ | Correlation $x_{i}^{\text {b }}$ | Value ${ }^{2}$ | Correlation x : |
| 8 | $12863.1338(45)^{\text {r }}$ | 8.218 | $12863.1347(45)$ | 8.205 |
| D | 0.048576231711 | 7.986 | 0.048 57681741 | 8.043 |
| $\lambda$ | 64.64931 | 4.410 | 25667.41871 | 3.955 |
| $\lambda_{D}$ | 0.0041611591 | 1.088 | 0.0064613681 | 1.137 |
| $\boldsymbol{y}$ | 2.7704761 | 3.889 | 2949(75) | 3.620 |
| $\gamma_{5}$ | -0.412640) | 11.774 | -0.3921391 | 1.547 |
| Rel. stad dev. | 1.017 |  | 1.056 |  |

## V. Discussion

Lines in the rotation spectrum of the NaC molecule in its ground " I $^{-}$state have been observed and finted satisfactorily with an effective Hamilonian to determine the appropriate molecular parameters. It is found that the two different seis of parameters fit the data equally well.

## A. Identification of the preferred parameter set

We have shown earlier that two solutions to the fitting problem are indeed expected from the form of the rotational energy levels for a molecule in a ${ }^{+5}$ - sate given in Eqs. (11)-(14). If the transitions with $\Delta J \neq \Delta N$ were detectable, it would be easy to identify the correct solution: unfortunately this is not the case for NaC at the present time. In the absence of this information, we have made an estimate of the spin-spin parameter $\lambda$ to help us decide between the solutions the most obvious difference between the fits is that one has a small value and the other a large value for this parameterl.

As is well known, ${ }^{24.29}$ the spin-spin parameter can be deseribed to a good accuracy by a first- and second-order term.

$$
\begin{equation*}
\lambda=\lambda^{(1)}+\lambda^{(2)} \tag{15}
\end{equation*}
$$

In order to estimate the values for $\lambda^{(1)}$ and $\lambda^{(2)}$, we consider the contributions from the ground and low-lying states of NaC . These states are the $\mathrm{X}^{+5}$ 部基e from the $\sigma \pi^{2}$ configuration, the $a^{2} \eta$ from the $\sigma^{2} \pi$ configuration and the $b^{2} A, c^{2} I^{*}$, and $d^{2} \Sigma-$ states from the $\sigma \pi^{2}$ configuration. The frst-order contribution $\lambda^{(1)}$ is the expectation value of the direct dipole-dipole operator for the $X^{4}$ - state. According to Lefebvre-Brion and Field. ${ }^{30}$ the value for $\lambda^{(1)}$ for a molecule in a ${ }^{+5}{ }^{-}$state coming from a $\sigma \pi^{2}$ configuration is zero in a LCAO approximation. Since we expect NaC to be ionic in character. the molecular orbitals are well approximated by atomic orbitals on the $\mathrm{C}^{-}$atom and the LCAO approximation is a good one.

The other contribution to $\lambda$ arises from second-order mixing of the $X^{4} \Sigma^{-}$state with excited clectronic states by spin-orbit coupling. Of the various low-lying states described above, only the $a^{2} \Pi$ and $c^{2} \Sigma^{+}$suates are involved because of the selection rules obeyed by the spin-orbit coupling operator. A simple calculation based on a representation of the $\pi$ and $\sigma$ molecular orbitals by $2 p$ orbitals on the $\mathrm{C}^{-}$atom ${ }^{31}$ gives the result
where $\xi$ is the atomic spin-orbit coupling parameter for an eleciron in a $2 p$ orbital on the $C^{-}$atom. The value of $s$ for $C$ is $27.5 \mathrm{~cm}^{-1}$. The value for $\mathrm{C}^{-}$is not known but is expected to be slightly smaller.) Since both the $a^{2} \Pi$ and $c^{2} \Sigma^{+}$ states correlate with a ${ }^{2} P$ state in the atomic limit, we take ${ }^{32.33}$

Substitution into Eq. (16) gives $\lambda^{(2)}=0.006 \mathrm{~cm}^{-1}$ or 190 MHz.

The conclusion of this estimate for the effective spinspin parameter $\lambda$ is that we expect ins value to be very small.

TABLE IV. Vabses for the rotational and fre-strucure parmeters deser-


| Parameter | Volue ${ }^{\text {a }}$ | Conrelation $\mathrm{n}^{\prime \prime}$ |
| :---: | :---: | :---: |
| $E$ | $8819.89651641^{\circ}$ | 3\%.4 |
| D | 0.02178074991 | 1817 |
| $10^{\text {x }} \mathrm{H}$ | 0.834481 | 599.3 |
| $\lambda$ | 175.81511 | 60.2 |
| $\lambda_{0}$ | $0.001+4371$ | 1.0 |
| $\gamma$ | 5.0472811 | $21: 2$ |
| $10^{2} \gamma_{D}$ | -0.64t601 | -1.2 |
| $\gamma_{s}$ | -0.052123 | 13.3 |
| Rel sud dev. | 0.359 |  |

Values in AHHz.
"Correlation parameter $x_{i}=\left(x^{-1}\right)_{11}$. where $x$ as the matrix of the correlation cocfficients.
The numbers in parentheses correspond to three ctandard deviations of the least squares fu.

Consequently, the least squares fit of the rotational frequencies of NaC which gives the small ralue for $\lambda 164.6 \mathrm{MHz}$, fit $A$ ) is to be preferred over fit $B$ which gives a large value for $\lambda(25.67 \mathrm{GHz})$. Admittedly. this choice is based on a rather crude estimate for $\lambda$ but in is supponed by the value for $\lambda$ determined for CH in its $a^{+5}$ state which is also rather small [2.786 GHz (Ref. 31 )]. A high quality ah initio calculation is really needed to support the assigment.

## B. Revised fit of the rotalional spectrum of KC in its $X^{4} \Sigma^{-}$state

The work described in this paper was preseded by the observation and analysis of the corresponding rotational spectrum of $K C$ in is $X^{45} 5^{-}$state. ${ }^{17}$ However, only one of the two possible solutions to the fitting problem was discovered at that time, namely, the one corrcsponding to the large value for $\lambda(17.03 \mathrm{GHz}$ in that case 1 . Because of their ionic character, both NaC and KC are expecied to have similar electronic structures. close to that of the $\mathrm{C}^{-}$ion. Thus all the arguments advanced in support of the small $\lambda$ fit of NaC apply equally well to KC. We have therefore taken the opportunity to refit the rotational frequencies of $K C$ to obtain the alternative preferred fil. The results are given in Table IV: the residuals oblained in this fit are broadly similar to those obtained earlier.

A comparison of the false fit ( $B$ ) for NaC with the corresponding one for KC reveals another aspect which lends supporn to the preference for the fits with the small values for $\lambda$. The large value of $\lambda$ for $\mathrm{NaC}(25.667 \mathrm{GHz})$ is bigger than the value for $\mathrm{KC}(17.033 \mathrm{GHz})$. This result is opposite to the one expected from the larger atomic spin-orbit coupling parameters for $\mathrm{K}\left(38 \mathrm{~cm}^{-1}\right)$ than for $\mathrm{Va}\left(11.5 \mathrm{~cm}^{-1}\right)^{30}$ Since the second-order spin-orbit mixing is proponional to the square of the effective coupling constant. it is expected to be larger for KC than NaC . This behavior is nicely illustrated by the spin-rotation parameters for the two molecules: the value of $\gamma$ for $\mathrm{KC}(5.047 \mathrm{MHz})$ is larger than that for NaC 12.770 MHzl, despite the smaller $B$-value.

TABLE Y. Vibraionad avernyed bond lenpths for alkali metal carbides.

| Molecute | Ground shate | $r_{0} / A$ |
| :---: | :---: | :---: |
| ${ }^{3} \mathrm{H}$ \% C | +5- | $223227580439)^{2}$ |
| 3SCC | ${ }^{45}$ | 2527943421924 |

The figures in promeheses represent the estimated uncertainty (lof in the bend lengets. in wiss of the lass quosed decinal place. The mumbers. whech are calculated from the standard error in the rotational comseant $B_{0}$. quesestimate the physical significance of these sumbers.

## C. Bond lengths for NaC and KC in their ground states

The primary piece of information from a rolational spectum of a diatomic molecule is the rotational constant and hence its bond length. The value for the zero-point band lengths, $r_{0}$, for NaC and KC in their $\mathscr{X}^{4 \Sigma}{ }^{-}$states are given in Table $V$. The value for KC is hardly changed from the value quoted earlier ${ }^{17}$ of $2.513 A$ : this is because the value for $B_{n}$ is determined by the leading term on the right-hand sides of Eqs. (11)-(14). The value for NaC is 2.232 A . The values in Table IV can be compared with the ionic radius of $\mathrm{C}^{-}(2.6 \AA)^{34}$ This radius is considerably larger than that of NaC or KC. Such a difference suggests that, alhough these two molecules are markedly ionic, they have not abandoned covalent behavior completely.

It is also interesting to compare the $\mathrm{Na}-\mathrm{C}$ bond lengths in $\mathrm{NaCH}_{3}$ and NaCH with that of NaC . Their values are $r_{\mathrm{Na}_{3} \mathrm{C}}=2.299 \AA$ and $r_{\mathrm{NaC}}=2.207 \AA$ for sodium monomechyl and sodium methylidyne. respectively. ${ }^{20,21}$ Clearly, the carbon atom in $\mathrm{NaCH}_{3}$ is $s p^{3}$ hybridized, while the hybridiza. tion in NaCH is $s p$. A simple picture of the bonding in NaC would suggest $s p$ hybridization at the carben atom. The fact that the NaC bond length lies somewhere between the values for molecules which show $s p$ and $s p^{3}$ hybridization suggests that the true situation in NaC may be $s p^{n}$ hybridized with $n>1$.

## Yi. CONClUSION

Spectroscopic data have been obtained for the sodium carbide radical for the first time. The data are in agreement
with theorcical expectations that the ground eiccronic state is ${ }^{4} I^{-}$. Analysis of the rotational spectrum shows that some uncertainty can anise in the determination of the spin-spin parameter in ${ }^{+5}$ slates. Although NaC is likely to be ionic. given the electron affinity of sodium relative so carbon. the derived bond length indicates some covalent character and perhaps even $s p^{3}$ hybridization of the unpaired ciectron orbitals.

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## APPENDIX: AMBIGUITIES IN THE ROTATIONAL ANALYSIS OF 'I STATES: HUND'S CASE (a) COUPLING

We have discussed the ambiguity in the fitting procedure of pure rotational transitions of a molecule in a +5 state, near the Hund's case (b) limit in Sec. IVB. The origin of this ambiguity can perhaps be more fully apprecialed by considening the general description of the energy levels. particularly when the molecule conforms most closely to a Hund's case (a) coupling scheme. As before. let us confine our attention to the Hamiltonian which includes the rotational kinetic energy, the spin-spin and spin-rotation coupling only.

We construct the matrix representation of this Hamiltonian in a parity-conserving basis sct.

$$
\begin{align*}
|J,|\Omega|: \pm\rangle= & (1 / \sqrt{2})\left\{\left|\Lambda^{s}: S \Sigma: J \Omega M\right\rangle\right. \\
& \left. \pm(-1)^{J-5 \div s}\left|-. \lambda^{5}: 5-\Sigma: J-\Omega M\right\rangle\right\}
\end{align*}
$$

where the upper and lower sign choices correspond to states of positive and negative parity respecrively and $s$ is even for $a^{+} \Sigma^{+}$state and odd for a ${ }^{+} \Sigma^{-}$state. The full matrix for a molecule in a ${ }^{4} 5^{s}$ state can be diagonalized into $2 \times 2$ blocks for each value of $J$ as follows:

$$
\begin{array}{ccc} 
& \left|J \frac{1}{2} ; \pm\right\rangle & \left\lvert\, J \frac{1}{3} \pm \pm\right. \\
\left|J \frac{3}{2} ; \pm\right\rangle & B\left[\left(J+\frac{1}{2}\right)^{2}-1\right]+2 \lambda-\frac{1}{2} \gamma & -\left(B-\frac{1}{2} \gamma\right) \sqrt{3}\left(\left(J+\frac{1}{2}\right)^{2}-1\right]^{1 / 2} \\
\left|J \frac{1}{5} ; \pm\right\rangle & \left.B\left[\left(J+\frac{1}{2}\right)^{2}+\frac{3}{3}\right]-2 \lambda-\frac{1}{2} \gamma \mp(-1)^{P} 2\left(B-\frac{1}{2} \gamma\right) \gamma j+\frac{1}{3}\right) .
\end{array}
$$

where $p=J-\frac{2}{2}+s$. In this matrix, the upper and lower sign choices give the states of positive and negative parity, respectively, for a molecule in a "Is state. The iwo levels with $s=1 / 2$ form a special case: their energies are given by the lower, diagonal element of the matrix. The two eigenvalues of the matrix are given by

$$
\begin{align*}
E_{=}= & B\left[\left(J+\frac{1}{\}}\right)^{2}+1\right]-\frac{5}{2} \gamma \mp(-1)^{\mu}\left(B-\frac{1}{2} \gamma i\left(J+\frac{1}{2}\right)\right. \\
& \pm \frac{1}{2}\left[\left\{4 \lambda-4 B+2 \gamma \pm(-1){ }^{n}\left(B-\frac{1}{2} \gamma\right)\left(J+\frac{1}{2}\right)\right\}^{2}\right. \\
& \left.+12\left(B-\frac{1}{2} \gamma\right)^{2}\left\{\left(J+\frac{1}{3}\right)^{2}-1\right\}\right]^{12} . \tag{2}
\end{align*}
$$

In this equation the $\pm$ sign choice in front of the square root gives the two eigenvalues; the $\pm$ sign choice in front of the phase factor $(-1)^{p}$ indicates the states of $\pm$ parity. The $J$-independen term inside the squase roo of Eq. (A2) is $(4 A-4 B+2 \gamma)^{2}$ and, provided this serm is large compared with $B^{2}(J+1 / 2)^{2}$, it makes a dominan contribution to the energy. In can be seen in this case that the parem of energy levels depends on the magnitude of the quantity ( $4 A-4 B$ $+2 \gamma$ ) but not its sign. There are two nearly identical solutions to the modeling problem depending on whether ( $4 \lambda$ $-4 B+2 \gamma$ ) is posidive or negative. Since the rouational constant $B$, which must be positive, is determined from the coefficient of $\left[(J+1 / 2)^{2}+1\right]$ in the leading term of Eq. (A2), the burden of the sign ambiguity is transferred to the parameter $\lambda$. It should be recognized also that $\gamma \leqslant \lambda$ in magnitude.

It should be appreciated that, although two different sets of parameters can give the same eigenvalues in Eq. (A2), the corresponding eigenfunctions will be distince. The correct choice of parameters can therefore be obtained from measurements of quantities which depend on the form of the eigenfunctions such as spectral line intensities or magnetic moments. The easiest way to solve this ambiguiry is to establish the position of the $J=1 / 2$ levels relative to those with higher $J$ because their energies depend directly on the sign of $A$. Unfortunately this solution to the problem is not always available in practice. The nature of the ambiguity described here is exactly the same as that encountered for molecules in ${ }^{2} 71$ states when the rotational eigenvalues depend quadratically on the quantity $(A-2 B) .{ }^{35}$

When $\lambda$ is comparable with $B$ in magnitude or even smaller, the ambiguous nature of the solutions in Eq. (A2) disappears. Thus we are more likely to encounter this ambiguity problem for molecules which conform to Hund's case (a) coupling ${ }^{36}$ than to Hund's case (b). As we know, both NaC and KC in their $X^{+5-}$ states show Hund's case (b) behavior. The ambiguity of the energy level scheme discussed in the Appendix is therefore not really appropriate to them. The energy levels schemes for the two possible values of $\lambda$ obtained in the fits of the NaC (and KC) data are disfinctly different from cach oher. The inability to disunguish between these iwo values arises because only a limited type of rotational transition has been detected. The transitions which would reveal the correct value of $\lambda$ are too weak to be observed.
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## APPENDIX F

## ROTATIONAL REST FREQUENCIES FOR CRO $\left(X^{5} \Pi_{r}\right)$ AND $\operatorname{CrN}\left(X^{4} \Sigma\right)$

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## ABSTRACT

The pure rotational spectra of $\mathrm{CrO}\left(x^{5} \Pi_{r}\right)$ and $\mathrm{CrN}\left(X^{\prime} \Sigma^{-}\right)$have been recorded using millimeter/sub-millimeter-wave spectroscopy in the frequency range $248-636 \mathrm{GHz}$. These radicals were created by the reac: tion of chromium vapor, produced in a Broida-type oven. with $\mathrm{N}_{2} \mathrm{O}$ or $\mathrm{NH}_{3}$, under DC discharge condinions. For CrO. 12 rotational transitions were recorded. in which up to five spin-orbit components were observedthe first measurement of the pure rotational spectrum of a molecule in a $\bar{\Pi} \|$ electronic state. Nine rotational transitions were recorded for CrN : here all four spin componenis were measured in every uransition. The data obtained for both radicals were analyzed using an appropriate effective Hamilonian. The resulting spectroscopic parameters of these species were determined to high precision. including those related to fine strucrure and lambda doubling. This work will enable radioastronomical searches for CrN and CrO to be carried out. CrO has already been observed in the optical spectra of stellar atmosphetes.
Subject headings: ISM: molecules - line: identification - methods: laboratory - molecular data

## 1. INTRODUCTION

Several small molecules containing metals (in the chemist's sensel have been detected to date toward the circumstellar envelopes of late-iype stars. in particular carbon-rich objects. For example. NaCl and AINC have been identified in the expanding shell of the $A G B$ star IRC +10216 (Cernicharo \& Guelin 1987: Ziurys et al. 2002), and NaCN and MgNC have been observed in the envelope of the post-AGB object CRL 2688 (Highberger el al. 2001). These species have all been identified in these sources on the basis of their pure rotational spectrum, observed using millimeter-wave telescopes. Crucial to these detections have been laboraiory measurements. in particular those at high spectral resolution te.g.. Robinson. Apponi, \& Ziurys 1997).

Given the observation of sodium-, magnesium- alumi-num-, and even potassium-bearing molecules in circumstellar gas. it is possible to contemplate species contaming other metals. One such metal is chromium, which is thought to be primarily produced in explosive silicon burning in supernovae (Woosley \& Weaver 1995). Nonetheless, it has a relatively large cosmic abundance compared to some of the other eariy iron group metals. For example, titanium has an abundance $\mathrm{Ti} / \mathrm{H} \sim 8.5 \times 10^{-8}$. while the $\mathrm{Cr} / \mathrm{H}$ ratio is $4.8 \times 10^{-7}$ (Savage \& Sembach 1996). The solar abundance of chromium is therefore only about a factor of 5 less than that of sodium and aluminum. Indeed. CrO is a known contributor to the electronic spectra found in stellar atmospheres (e.g., Davis 1947). However. thus far. chromiumbearing molecules have not been observed in circumstellar gas primarily because there has been a dearth of high-resolution laboratory data for such small. astrophysically relevant species. Although several possible chromium compounds have been investigated via their electronic transitions at optical wavelengths (Bames. Hajigeorgiou. \& Merer 1993: Balfour. Qian. \& Zhou 1997). these studies have not had sufficient resolution to determine spectroscopic constants that can reproduce millimeter/submilli-
meter transition frequencies with the necessary accuracy for astronomical searches ( $<1 \mathrm{MHz}$ ). Therefore. interstellar studies of Cr -bearing molecules have been extremely limited.

Two molecules of astrophysical interest are CrO and $\mathrm{Cr} N$. Both species have been the subject of several previous spectroscopic investigations. For example. Merer and co workers measured the $\left.{ }^{5} \Sigma^{+}-\lambda^{5} \cap\right], \Delta-\lambda^{\prime} \leq \Pi$. and $511-\lambda$ : electronic transitions of CrO with rotational resolution (Hocking et al. 1980; Cheung. Zyrnicki. \& Merer 1984: Barnes et al. 1993). Their studies also involved further development of the specific Hamiltonians necessary to describe these quintet electronic states. In addition, the permanent electric dipole moment of CrO was mensured using optical stark spectroscopy (Steimle et al. 1989). The CrN radical was first investigated by $a b$ initio and density functional theory (DFT) merhods. which predicted a ${ }^{5} \Sigma^{-}$ground electronic state (Harrison 1996; Andrews. Bare. \& Chertihin 1997). This prediction was confirmed by the measurement of the $A 4 \Pi-\lambda{ }^{4}$ - transition using laser-induced fluorescence (LIF) spectroscopy (Balfour et al. 1997). Furthermore. the permanent electric dipole moment was measured. as well as fine and hyperfine parameters using data obtained by pump/probe microwave-optical double-resonance (PPMODR) iechniques (Sieimle. Robinson. \& Goodridge 1999: Namiki\& Steimle 1999).

In this paper we report the first measurements of the pure rotational spectrum of both CrO and CrN in their respective $\lambda^{3}{ }^{3}$, and $X^{4} \Sigma^{-}$ground electronic states. The purpose of this work was to directly record rotational transitions of these radicals for astronomical identification at millimeter/ submillimeter wavelengths. The molecules were sudied using direct-absorption methods in the frequency range $248-636 \mathrm{GHz}$. For both species. fine-structure splitings were resolved. and in the case of CrO. Jambda-doubling interactions as well. These data have been analyzed to produce a revised set of spectroscopic parameters for these molecules. Here we present our resulis.

## 2. EXPERIMENTAL

The pure rotaional spectra of CrO and CrN were measured using one of the millimeter/submillimeter-wave spectrometers of the Ziurys group (Ziurys et al. 1994). The instrument consists of a set of phase-focked Gunn oscillators and Schortky diode multipliers shat produce radiation over the frequency range $65-650 \mathrm{GHz}$. a double-walled. water-cooled. sieel reaction chamber containing a Broidapype oven, and an InSb bolometer delector cooled to approximately 4 K . The radiation is launched from the source as a Gaussian beam. directed into the reaction cell via a set of offset ellipsoidal mirrors, and passed into the reaction chamber through a polystyrese uindow. At the rear of the cell. a rooftop reffector rotates the plane of polarization of the radiation by $90^{\circ}$ and propagates it back through the cell and optics into the detector. Phase-sensitive detection is employed using FM source modulation.

CrO was produced by the reaction of chromium metal vapor with $\mathrm{N}_{2} \mathrm{O}$. The vapor was created in a high-temperature Broida-iype oven. packed with alumina and zirconia insulation to achieve the necessary high iemperatures. Approximately $10-15$ mtorr each of $\mathrm{N}_{2} \mathrm{O}$ and argon. the carrier gas used to entrain the metal vapor. were introduced into the reaction chamber through the bottom of the oven. A DC discharge was not required to produce CrO: however. use of a discharge enhanced the synthesis of the molecule ( 0.01 A at 200 V ). CIN was created by an identical method. except that $\mathrm{NH}_{5}$, was substituted for $\mathrm{N}_{2} \mathrm{O}$ and a discharge was required with higher current ( 0.7 A ).

For both molecules. rotational transitions were recorded over the frequency range $248-636 \mathrm{GHz}$. Line widths ranged from 600 kHz at 248 GHz to 1700 kHz at 636 GHz . Final frequency measurements were obrained by fiting Gaussian curves to the line profiles. These profiles consist of averages of one to six scan pairs. 5 MHz in coverage. with an equal number increasing and decreasing in frequency.

## 3. RESULTS

The iransition frequencies measured for CrO are presented in Table 1: in all. 12 rotational were recorded. The ground state of CrO is ${ }^{5} \mathrm{M}_{r}$. and therefore the spectra are complicated by the presence of $L \cdot S$ coupling, which splits every rotational transition into five spin-orbit components. labeled by the quantum number $\Omega$. This quantum number is the sum of the projection of the electron orbital angular momentum along the internuclear axis. l. and the projection of the electron spin angular momentum. $\Sigma$. i.e.. $\Omega=A+\Sigma$ as is appropriate for a Hund's case (a) coupling scheme. Since $|A|=1$ and $S=2$ in a 5 state. $\Omega$ takes on the values $-1,0,1,2$, and 3 : hence, five sublevels are created. In addinion. there can be further splitings in every $\Omega$ component due to lambda-doubling interactions, which are porentially present in every degenerate electronic stase. This effect can split each $\Omega$ level into doubless. which are labeled by the parity notation $e$ and $f$.

As shown in Table 1, both spin-orbit and lambda-doubling interactions were observed in the data recorded for CrO . In six of the 12 rotational transitions. all five spin-orbit components were observed and their frequencies measured. (Poor signal-io-noise ratio in the spectra or gaps in the multiplier coverage prevented observation of all five sublevels in every transition.' Lambda-doubling interactions were also
resolved in all spin-orbin components excent for the ? sublevel. The $e$ and I parity labels were assigned assuming that the dominant perturber is the $A 5{ }^{-}$state: Bauschlicher. Nelin. \& Bagus 1985.) For the $!=0$ sublevel. the spliting was the largest ( $500-700 \mathrm{MHz}$ ) and was found to increase with increasing $J$ quantum number. For the $\Omega=1$ 2. and 3 components the lambda doubling successively decreased in magnitude. although for the individual sublevels there was an increase in the splitting with $J$. The opposite effect was observed for the $\Omega=-1$ sublevel. where the separation decreased with $J$. such that it was only a few MHz at the $J=19-18$ transition.

Figure 1 show's a srick spectrum of the $J=16-15$ rota tional transition. which covers the range $-485-517 \mathrm{GHz}$. The experimentally observed intensities are also shown in the diagram. as are the lambda-doubling splittings. The total splituing of the $\mathbb{Q}$ sublevels in frequency space in this transition is rather large-almost 32 GHz . which is about twice the rotational constant. However, the splitting between the components is fairly regular. The spin-orbit component lying lowest in frequency corresponds to the one that is lowest in energy, $\Omega=-1$. About 9 GHz higher in freguency is the $\Omega=0$ sublevel. followed by $\Omega-1,2$, and 3 . Because each successive spin-orbit component lies higher in energy by $\sim 63 \mathrm{~cm}^{-1}$. the intensity slowly decreases for $\Omega>0$. (The $\Omega=3$ line is stronger than the $\Omega=1$ and 2 features only because there is no lambda doubling: thus. this line gains a factor of 2 in intensity.)

Figure 2 displays representative spectra of CrO near 486 GHz. Here the $\Omega=-1$ sublevel of the $J=16-15$ transition is shown. along with the $\Omega=3$ component of the $J=15-14$ transition. The effects of lambda doubling are evident in the $\Omega=-1$ line. which is split into doublets. In the $\Omega=3$ feature. such effects are negligible and it appears as a single line. increasing its intensity relative to the other component.

Table 2 presents the measured transition frequencies for CrN in its ground ${ }^{45}$ - electronic state. Data for nine rotational transitions were recorded over the frequency range $294-636 \mathrm{GHz}$. The spectra are complicated because of the


Fig. 1.-Stick spectrum of the $J=16-15$ transuion of CrO . All five spin-orbit components are shown with their approximate neasured intensities. Their reqular bur wide $(\sim \bar{i}-9 \mathrm{GHz})$ spacing is apparent. The $\Omega=0$ and 1 spin-orbil components are splin by lambda-ivpe doubline into two well-separated tines, while this effect is stmather in the $?=-1$ and 2 componems. The $\Omega=3$ spin-orbia componem appears as the strongest feature since the tanbia doublets are collapsed into a single time.

TABLE:
Measured Rotational Travsition Frequencies for


| $j+1-j$ | $\Omega$ | Parity | 1 uts | $\nu_{\text {che }}-\nu_{\text {cinh }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 8-7.......... | 0 | r | 247.587.324 | 0.035 |
|  | 0 | I | 388.019 .651 | -0.024 |
| $\cdots$ | 1 | c | 952.162.958 | -0,089 |
|  | 1 | , | 251.811.23? | -0.084 |
|  | 2 | i | 253.710 .397 | -0.028 |
|  | 2 | f | 255.701 .467 | 0.015 |
|  | 3 | * | 259.184.975 | -0.008 |
|  | 3 | f | 250.184.075 | 0.020 |
| 9.-8........... | $-1$ | c | 273.231.540 | -0.001 |
|  | $-1$ | $f$ | 273.181 .301 | -0.007 |
|  | 0 | $r$ | 278.534.967 | 0.012 |
|  | 0 | j | 379.009 .559 | -0.031 |
|  | 1 | e | 283.659.746 | 0.030 |
|  | 1 | f | 283.274.706 | -0.035 |
|  | 2 | c | 287.649.794 | -0.021 |
|  | 2 | $f$ | 2\$7.637.182 | -0.002 |
|  | 3 | e | 291.551 .121 | -0.032 |
|  | 3 | f | 291.551 .121 | 0.030 |
| 10ヶ9 ......... | -1 | \% | 303.607.735 | 0.004 |
|  | -1 | $f$ | 30. $5.56 .26 ?$ | -0.006 |
|  | 0 | 1 | 209.482.234 | 0.0 .39 |
|  | 0 | f | 309.995.245 | -0.011 |
|  | 1 | $c$ | . 315.148 .286 | 0.015 |
|  | 1 | f | 314.733.448 | -0.031 |
| 11-10....... | -1 | ${ }^{\circ}$ | 335.988.891 | <0.00\% |
|  | -1 | $f$ | 133.937.489 | 0.011 |
|  | 0 | ${ }^{\text {a }}$ | 340.428.850 | 0.026 |
|  | 0 | $f$ | 340.976 .285 | -0.006 |
|  | 1 | \% | 346.627 .973 | 0.032 |
|  | 1 | $f$ | 346.186.991 | -0.032 |
|  | 2 | c | 351.502 .035 | 0.019 |
|  | 2 | f | 351.479.606 | -0.036 |
|  | 3 | - | 356.248 .848 | -0.069 |
|  | 3 | f | 356.248 .848 | 0.070 |
| 12-11...... | $-1$ | \% | 374.375.388 | -0.007 |
|  | -1 | f | 364.325 .292 | -0.018 |
|  | 0 | ' | 371.374.70. | -0.015 |
|  | 0 | r | 371.952.340 | 0.004 |
|  | , | c | 378.097 .986 | -0.007 |
|  | 2 | 1 | 383.412 .907 | -0.100 |
|  | 9 | $j$ | 383.384 .496 | 0.009 |
|  | 3 | . | $388.578 .080^{\mathrm{b}}$ | -0.139 |
|  | 3 | $f$ | $388.578 .080^{\text {b }}$ | 0.085 |
| $13-12 \ldots \ldots$ | -1 | t | 394.767.594 | 0.014 |
|  | -1 | ! | 394.720 .047 | -0.030 |
|  | 0 | c | 402.319.707 | 0.038 |
|  | 0 | j | 402.923 .057 | 0.004 |
|  | 1 | : | 409.557.772 | 0.083 |
|  | 1 | $i$ | 409.076 .184 | 0.003 |
|  | $?$ | i | 415.212 .783 | 0.013 |
|  | 2 | $j$ | 415.277.240 | 0.044 |
|  | 3 | i | 420.892.769 ${ }^{\text {t }}$ | -0.180 |
|  | 3 | $f$ | 420.892.769 ${ }^{\text {b }}$ | 0.132 |
| 14-13....... | 1 | \% | $441.0 \times 6.513$ | 0.024 |
|  | 1 | $f$ | 440.510 .592 | -0.044 |
|  | 2 | $i$ | 47.200 .388 | 0.081 |
|  | 2 | $i$ | 447.156.920 | 0.028 |
|  | $?$ | \% | $453.191 .756^{\text {b }}$ | -0.279 |
|  | 3 | $j$ | 453.191.765 ${ }^{\text {b }}$ | 0.165 |
| 15-14....... | -1 | i | 455.509 .497 | -0.005 |
|  | $-1$ | f | 455.531.352 | 0.020 |
|  | 0 | $i$ | 2504, 205.828 | -0.003 |
|  | 0 | $i$ | +64.447.262 | $<0.000$ |
|  | 1 | - | 472.443.66? | 0.013 |

TABLE 1-Cintinued

| $J+1-J$ | 9 | Parisy | $\nu_{0}$ cts | $\nu_{\text {ubs }} \cdots \nu_{\text {and }}$ |
| :---: | :---: | :---: | :---: | :---: |
| 15-14....... | 1 | $f$ | 471.937.669 | 0.087 |
|  | 2 | ' | 479.074.839 | -0.0.3 |
|  | $?$ | $f$ | 479.097.766 | 0.041 |
|  | 3 | - | 253.474.018 ${ }^{4}$ | -0.43 |
|  | 3 | f | $48.474 .018{ }^{4}$ | 0.202 |
| 16-15...... | -1 | - | 485.979.644 | -0.022 |
|  | -1 | 1 | 485.948.120 | 0.003 |
|  | 0 | * | 495.146.531 | 0.012 |
|  | ${ }^{6}$ | f | 445.800 .196 | 0.016 |
|  | 1 | ' | 503,858.636 | 0.017 |
|  | 1 | i | 503.356.501 | 11.024 |
|  | 2 | ' | \$10.935.551 | -0.024 |
|  | 2 | f | 510.873 .877 | 0.0014 |
|  | 3 | ' | 517.73.574 | -0.50i |
|  | 3 | $i$ | $517.738 .574^{\text {b }}$ | 0.329 |
| 17-16....... | -1 | ${ }^{\prime \prime}$ | 516.996 .106 | 0.042 |
|  | -1 | f | 516.372 .421 | -0.005 |
|  | 0 | ' | 526.085.209 | -0.009 |
|  | 0 | f | 526.746 .800 | -0.019 |
|  | 1 | c | 535.280 .804 | -0.015 |
|  | 1 | $i$ | 534.766.66.3 | 0.037 |
|  | 2 | c | 542.781 .637 | 0.054 |
|  | 2 | 1 | 542.769 .5 (64 | 0.025 |
| 18-17....... | 2 | $p$ | 574.612.008 | -0.072 |
|  | 2 | $i$ | 574.528.989 | 0.031 |
| 19-18 | -1 | ' | 571.247.575 | -0.024 |
|  | -1 | j | 577.24i.515 | 0.025 |
|  | 0 | $\cdot$ | 587.955.228 | -0,086 |
|  | 0 | f | 588.619 .119 | 0.037 |
|  | 1 | $r$ | 598.064 .947 | -0.6.2 |
|  | 1 | $i$ | 597.358.428 | 0.649 |
|  | 7 | r | 606.426 .279 | 0.014 |
|  | 2 | $i$ | 006.31.35 | -6.03\% |

$-\operatorname{In} \mathrm{MH}_{2}$

- Not included in fit.
presence of three unpaired electrons in this molecule. The resultant spin angular momentum couples with the molecular frame rotation. indicated by quantum number $N$. to produce fine structure. labeled by $J$. where $J=N+S$. Four fine-structure components are therefore generated per rotational level. and all four were recorded in every transition. The separation between the fine-structure components was found to decrease with increasing $N$. such that the toid separation is $\sim 6 \mathrm{GHz}$ in the $N=8 \leftarrow 7$ rotational transition. decreasing $80 \sim 1.6 \mathrm{GHz}$ in the $N=17-16$ lines.
In Figure 3 a iypical spectrum for CrN is shown. illustrating the fine-structure splittings. Here all four spin components of the $N=13-12$ rotational transition near 484487 GHz are displayed. necessitating a trequency gap in the specirum. The fine-siructure lines are not eveniy spaced. and the $\Sigma=3 / 2$ component $(J=14.5-13.5)$ lies lower in frequency than that corresponding to $5=\frac{1}{5} \quad(J=$ $13.5-12.5)$. These two components actually shift relative to each other as a function of $N$.
A diagram illustrating the shift of the fine-structure components is presented in Figure 4. Here stick figures of the $N=9-8.12-11$ and $17-16$ transitions arc shoun. For the $N=9 \leftarrow 8$ transition, the $\Sigma=3 / 2$ component lies almost 0.5 GHz lower in frequency relasive to the $5=\frac{1}{2}$ hine, but the separation successively narrows such that at the $N=17-16$ transition. it actually hes at higher frequency.


Fic. 2.-Spectram showing the $9=-1$ componeat of the $J=16-15$ transition and the $\Omega=3$ line in the $J=15-14$ transition of $\mathrm{CrO}\left(Y^{5} \mathrm{II}_{f}\right)$. measuret in the taboratory near 486 GHz . The lambda doubling is seen in the $\Omega=-1$ spin-orbit component. which is split into two separate features. The lambda-type doubling in the $\cap=3$ component is not resolved and therelore appears as a single line. This spectrum is a composise of six seans. each 100 AHz in frequency coverage, and acquired in 1 minute.

The other components are moving closer to each other as well. such that at very high $N$. a nicely spaced quartet would be expected per transition. similar to KC (Xin \& Ziurys 1999). The change from an irregular quartet to a regular one occurs because of a term in the energy eigenvalues roughly proportional to $\lambda^{2} / N$. which becomes progressively less important as $N$ increases (see Sheridan et al. 2002 for detailsi. At this point. the constant governing the separation of the spin components is $\%$, the spin-rotation parameter.

## 4. ANALYSIS

The data for the $\lambda^{3} \Pi_{r}$ state of CrO were analyzed using an effective Hamiltonian in a case (a) basis, which consists of five basic interactions:

$$
\begin{equation*}
\dot{H}_{\mathrm{eff}}=H_{\mathrm{rol}}+\dot{H}_{\mathrm{so}}+\dot{H}_{\mathrm{si}}+\dot{H}_{\mathrm{sr}}+\dot{H}_{\mathrm{ld}} . \tag{1}
\end{equation*}
$$

The first term deals with molecular frame rotation. the next three with spin-orbit. spin-spin. and spin-rotation couplings, and the final term with lambda doubling. Centrifuga! distortion corrections are included in each interaction. Standard forms of $H_{\text {rot }}, \dot{H}_{\mathrm{so}}, \dot{H}_{\mathrm{ss}}$, and $\dot{H}_{\mathrm{sr}}$ can be found elsewhere (Browner al. 1979: Barnes ct al. 1993). The spin-orbit Hamilonian also involves the coupling between this term and the spin-spin interaction (Brown et al. 1981), characterized by the constant $n$. i.e..

$$
\begin{equation*}
\dot{H}_{s o}^{(3)}=\eta L_{:} S_{:}\left(S_{5}^{2}-\frac{3 S^{2}-1}{5}\right) \tag{2}
\end{equation*}
$$

The lambda-doubling Hamiltonian. which includes centrifugal distortion, takes on the form (Barnes et al. 1993)

$$
\begin{align*}
\hat{H}_{\mathrm{ld}}= & \frac{1}{2}(o+p+q)\left(S_{-}^{2}+S_{-}^{2}\right)-\frac{1}{2}(p+2 q)\left(J_{+} S_{-}+J_{-} S_{-}\right) \\
& +\frac{1}{2} q\left(J_{-}^{2}+J_{-}^{2}\right)+\frac{1}{2}(0+p+q)_{D}\left(S_{-}^{2}+S_{-}^{2}\right) \cdot R^{2} \\
& -\frac{1}{2}(p+2 q)_{D}\left(J_{-} S_{-}+J_{-} S_{-}\right) \cdot R^{2}+\frac{1}{2} q_{D}\left(J_{-}^{2}+J_{-}^{2}\right) \cdot R^{2} . \tag{3}
\end{align*}
$$

TABLE :
Measergid Rotathonal Thanation Frequenciesfor $\operatorname{CrN}\left(\mathrm{X}^{+5}-\mathrm{I}^{4}\right.$

| $N^{+}+1 \cdots$ | $J+1-1$ | Lints | $v_{\text {utib }} \cdot t^{*}$ and |
| :---: | :---: | :---: | :---: |
| 8-7............ | 6.5-5.5 | 294.381.337 | -0.608 |
|  | 7.5-6.5 | 297.596.35 | -6.0.11 |
|  | 8.5-7.5 | 301.653 .358 | -0.010 |
|  | 9.5-8.5 | 300.509.832 | -6.0.6) |
| 9-8............ | 7.5-6.5 | 332.98 .177 | 0.025 |
|  | 8.5-7.5 | 395.238.997 | 0.086 |
|  | 9.5-8.5 | 388.587 .895 | 0.005 |
|  | 10.5-9.5 | ? 7.233 .576 | 0.024 |
| 10-9 ........... | 8.5-7.5 | 371.150 .45 | 0.005 |
|  | 9.5-8.5 | :72.810.113 | -0.010 |
|  | 10.5-9.5 | 375.5783 | nomes |
|  | 11.5-10.5 | $: 74.943 .139$ | -0.003 |
| 11-10........ | 9.5-8.5 | 409.057 .72 | 0.001 |
|  | $10.5-9.5$ | +10.328.231 | 0.001 |
|  | 11.5-10.5 | +12.655.30\% | 0.001 |
|  | 12.5-i1.5 | 412.249.292 | -0.009 |
| $12-11 \ldots$ | 10.5-9.5 | 476.798 .340 | -0.030 |
|  | $11.5-10.5$ | 47.805 .158 | 0.011 |
|  | 12.5-11.5 | 449.798 .189 | 0.019 |
|  | 19.5-12.5 | +49.535.996 | $<0.000$ |
| $13-12 \ldots \ldots \ldots$ | 11.5-10.5 | 4.4.426.450 | -01.00\% |
|  | 12.5-11.5 | 485.248.70.1 | 0.007 |
|  | 13.5-12.5 | 486.980 .640 | 0.024 |
|  | 14.5-15.5 | \$86.806.09.5 | -6.033 |
| $14-13 \ldots \ldots$ | $12.5-11.5$ | 521.974 .902 | $<0.006$ |
|  | 13.5-12.5 | 529660.049 | -0.009 |
|  | 14.5--13.5 | 524.188 .137 | 0.015 |
|  | 15.5-14.5 | 524.087.936 | -0.011 |
| $16-15 \ldots \ldots$ | 14.5-13.5 | 596.906. 399 | -0.010 |
|  | 15.5-14.5 | 597.429.959 | -0.0618 |
|  | 16.5-15.5 | 598,641.015 | -0.062 |
|  | $17.5-16.5$ | 598.692.991 | 0 ORix |
| $17-16 . . . . . .$. | 15.5-14.5 | 6.3 .4 .310 .973 | 0.010 |
|  | 16.5-15.5 | 63.4 .770 .366 | 0.015 |
|  | $17.5-16.5$ | 615.874 .043 | $0.60 \cdot$ |
|  | $18 \leq-17.5$ | 635.911 .409 | -0.02\% |

a In Milz.

Three constants ( $o, p$, and $q$ ) are thus required to describe lambda doubling in $\because \Pi$ states.
For CrN , the Hamitonian used to analyze the data consists of rotarional, spin-rotation. and spin-spin terms (Nelis. Brown. \& Evenson 1990):

$$
\begin{equation*}
H_{\mathrm{ef}}=\dot{H}_{\mathrm{rel}}+H_{\mathrm{ss}}+\dot{H}_{\mathrm{ss}} \tag{4}
\end{equation*}
$$

Included in the spin-rotation coupling is the third-order correction to this interaction. which in a case (b) basis is best expressed in tensor form:

$$
\begin{equation*}
\left.\dot{H}_{\mathrm{sr}}^{3}=\left(\frac{10}{\sqrt{6}}\right)\right)_{1}^{3}\left(L^{2} . N\right) \cdot \mathrm{T}^{3}(S .5 . S) \tag{5}
\end{equation*}
$$

This term is thought to be necessary to describe the spinrotation coupling in states whit quartet multiplicity or higher (Hougen 1962).

Using these respective Hamiltonjans, the two data sets were analyzed using a least-squares fitting routine. The spectroscopic parameters determined from these fits are given in Tables 3 ( CrO ) and $4(\mathrm{CrN})$. As the tables show. all


Fig. 3.-Laboratory spectrum of the NE $^{6}=13-12$ rotational transition of CrN $4 \mathrm{Y}^{-2-1}$ metr $484+487 \mathrm{GHz}$. There is a frequency gap in the data of of CrN $\mathrm{CY} \mathrm{Y}^{2-}$ ) mear $484-487 \mathrm{GHz}$. There is a frequency gap in the data of
1.4 GHz . Here all four fine-srucure components. indicated by quantum 1.4 GHz . Here all four fine-sirucrure components. indicated by quantum
number $/$. are visible. (Their reiative intensities are not all the same onty number J. are visible. Their reiative intensities are not all the same onty
because of variations in production efficiency.) The line corresponding to because of variations in production efficiency.) The line corresponding to
$\Sigma=3 ; 2(J=14.5-13.5)$ lies iower in frequency relative to the $\Sigma=\frac{1}{2}$ feature $\{J=13.5-12.5)$. The spectrum is a composite of 16 scans. each 100 MHz in frequency width. and recorded in $\sim 1$ minute.

Constants used in the analysis are well determined. and the rms values of the fits are $39(\mathrm{CrO})$ and $23 \mathrm{kHz}(\mathrm{CrN})$.

In the case of CrO. the spectroscopic constants established from optical LIF data are included in Table 3 for comparison. These parameters were qaken from Barnes et al. (1993), who studied the $A^{\prime}{ }^{5} \Delta-X^{\prime}$ ill systems using LIF and combined their result with Fourier transform infrared emission spectra. As shown. the millimeter-wave constants established in this work are in good agreement with those of Barnes et al. (1993) but improve the accuracy of the roiational. lambda-doubling, and some of the fine-structure values. There are some difierences as well. For example. in the current study, the centrifugal distortion terms $\mu_{D}$ and $\eta_{D}$ were not found to improve the overall rms of the fit and were therefore not included in the final analysis. On the other hand. the higher order spin-spin interaction term. $\theta$, was found to be necessary for a good fit. It should also be noted that the constants $\gamma$ and $A_{D}$ are highly correlated with each other, and consequently it is difficult to establish their values accurately in the analysis (Brown et al. 1979). Finally, rotational transitions with $J>10$ originating in the $\Omega=3$ spinorbit components were not included in the least-squares fit. Lambda doubling was not resolved in this component, and at high $J$, where this effect was substantial in other $\Omega$ sublevels. large residuals were generated ( $\sim 500 \mathrm{kHz}$ ) for these features. Despite the exclusion of these transitions. 84 individual lines were included in the final analysis.

For CrN. the millimeter-wave consiants determined in this study are in agreement with the LIF/PPMODR values. which are given in Table 4 (Namiki \& Steimle 1999). There appears to be a factor of 2 difference and a sign change in the value of the spin-rotation interaction parameter is between the two fis. however. On the other hand. the analysis dome in this work employs three spin-rotation parameters ( $\gamma, \gamma_{D}$. and $\gamma_{i}$ ), while the previous study only used $\gamma$ and \%.s. Moreover, the data set from the previous work is not


Fig. 4.-Slick sperira of three separate rotational transitions of CrN. iliussrating the progression of the fine-structure splittings, It the top panel. thestrating the progression of the fine-structure spintings. In the top pand. the spin components of the $\hat{N}=9-8$ rotaional innsmon have a toral separation of over 6 GHz with the $\Sigma=3,2$ line hing lower in frequency that its $\Sigma=\frac{1}{4}$ counterpart. In the $\lambda=12-11$ transifion. the fine-struclure lines are distributed over only 3 GHz and the $\Sigma=3 / 2$ and $\Sigma=\frac{1}{2} \mathrm{spin}$ components lie cioser in frequency. Finatly in the $N=17-16$ ransition. the fine-siructure quarte has coliapsed to a total separation of 1.6 GHiz. Now the $\Sigma=\frac{1}{2}$ component is fower in frequency than she $\mathrm{E}=3,2$ line.
nearly as extensive. Some variations are therefore expected. In addiion, the marrix elements for the third-order spinrotation term have some subule differences. depending on the basis set, as discussed by Adam et al. (1994). Here those of Nelis et al. (1990) were used. in a case (b) basis. Namiki \& Steimle (1999) modified those of Adam et al. (1994). which thilized a case (a) basis set. (The theory and interpretation behind the is term are not well developed because it is required only for high spin states. of which there are few examples studied al high resolution.)

## 5. DISCUSSION

The primary result of this invesigation is that very accurate rotational rest frequencies have been directly measured for CrO and Cr N in their ground electronic states in the submillimeter region. (The complicated ground states exhibited by these two radicals make direct measurements desirable.) The spectroscopic constants of both these radicals have additionally been refined. Moreover. this work is the first time a molecule in a $5 \pi$ ground state has been sudied by

TABIE ?


| Parameser | Aillimeter Wave | Oplical ${ }^{\text {a }}$ |
| :---: | :---: | :---: |
| B................. | 15722.0298115) | 15722.003) |
| D.................. | $0.02184644846)$ | $0.0219(1)$ |
| Y .................. | $315213)$ | 36.1121 |
| $A_{D} \ldots \ldots . . . . . . . . . . .$. | -4.43.3.6) | $-3.60424)$ |
| A.................. | $1894999+3 \times 1$ | 1895690 30 ) |
| $(0+p+q) \ldots$ | 998.38.8) | 95\%6) |
| $(p+2 q) \ldots . . . . .$. | 206.53(46) | 20911 |
| 4.................. | -1.0313) | -1.3(1) |
| $10+p+9.0 \cdots$ | -0.071(21) | -0.093(12) |
| $(p+2)_{0} \ldots \ldots$ | -0.00254(17) | 0.002412) |
| 40............... |  | $0.00011(8)$ |
| $\lambda$.................. | 344076361) | $34683(15)$ |
| $\lambda_{D} \ldots \ldots \ldots \ldots \ldots \ldots$ | -0.052113) | $0.0666(12)$ |
| 刀.................. | -2302.09.4) | $-2940107$ |
| 70................ | ... | -0.27(4) |
| H................... | 4.67(94) | ... |
| rms................ | 0.039 | 42 |

perre rotational spectroscopy. Thus, if serves as a test of angulat momentum coupling theory
Both $\mathrm{Cr} N$ and CrO exhibir high spin siates, which arise from unusual electron configurations. The primary valence electron confguration of the ground siate of CrN is $8 \sigma^{2} 3 \pi^{4} 9 \sigma^{1} 18^{2}$ (Balfour et al. 1997) and of the ground siate of CrO is $8 \sigma^{2} 3 \pi^{4} 9 \sigma^{1} 1 \delta^{2} 4 \pi^{1}$ (Barnes et al. 1993). In these configurations, the $8 \sigma$ and $3 \pi$ are bonding molecular orbitals formed primarily from the $3 d_{r}$ and $3 d_{\pi}$ atomic orbitals on chromium and the $2 p_{c}$ and $2 p_{\pi}$ atomic orbitals from oxygen or nitrogen. with the $4 \pi$ and $10 \sigma$ as the corresponding antibonding ones. The $9 \%$ and $1 \delta$ molecular orbitals arise predominately from the 45 and $3 d_{5}$ atomic orbitals of chromium. respectively, and they both are almost completely nonbonding.
If the $4 \pi$ orbial is actually antibonding, addition of an electron to this site should increase the bond length of CrO relative to $\mathrm{Cr}_{\mathrm{I}} \mathrm{N}$. Indeed, this increase does occur. From the millimeter-wave data, the $r_{0}$ bond lengths of the CrN and CrO radicals were determined to be 1.5652 and $1.6213 \AA$. respectively, resulting in a bond lengthening of $0.0561 \AA$ for the oxide compound. Such an increase appears to generally occur for $3 d$ transition metal oxides relative to the nitrides, independent of the filling of orbitals. For example. VN has a

TA明E
Rotational Constants Determanedrom CrAi.iss-1

| Parameter | Millimeter Waven | PPMSODR/Opricatit |
| :---: | :---: | :---: |
| B.............. | 18702.90551 ${ }^{\text {(4) }}$ | 18702.952437) |
| D............... | $0.631854 .43)$ | $0.01558(75)$ |
| \% ............... | $209.361(47)$ | $3(4) .53365)$ |
| To............ | $0.000291(64)$ |  |
| 7 7, .............. | $0.1328(85)$ | -0.235(22) |
| $\lambda$............... | 78281.97(58) | 78281.32(21) |
| $\lambda_{0} \ldots . . . . . . . . .$. | -0.21744(56) | ... |
| mms............ | 0.029 | $\ldots$ |
| 4 in MH2 <br> ${ }^{\circ}$ From N LIF data. ex | ors are ia. <br> is Steimle 1999: me <br> ag hyperine terms. | ed Et of PPMODR and |

bond length of 1.566 A (Balfour et al. 1993). While that of VO is 1.592 A (Merer 1989). A very similar difference is also seen in FeN yersus FeO (P. M. Sheridan. T. Hirano. \& L. M. Ziurys 2002, in preparation; Allen. Ziarys. \& Brown 1996) and TiN versus TiO (Namiki eq al. 1998). This general result most likely occurs because the $2 p$ atomic orbitals of nitrogen are nearly $24.000 \mathrm{~cm}^{-1}$ higher in energy than those of oxygen. Thus, there is a smaller energy gap between the nitrogen orbitals and the 3 at atomic orbitals of the metal. which enables a stronger bond to form in the nitride as compared to the corresponding oxide.

Chromium oxide is most likely to be found in O-rich circumstellar envelopes such as OH 231.8. Searching for rotalional lines in the $\Omega=-1$ component, which lies lowest in energy and exhibis small lambda doubling. is likely the best approach. CrN , on the other hand. may be detectable in shells of carbon-rich stars, including IRC +10216 or CRL 2688. Metal cyanide species have already been observed in these objects. and a nirtide compound may also be feasible. given the presence of SiN in IRC +10216 (Tumer 1992). Observation of the four spin components within a single rotational transition should be sufficient evidence for identification of this radical. given the large frequency separation of these lines. Boih CrO and CrN also have relatively large dipole moments as well ( 3.88 D . Steimle et al. 1989: 2.31 D. Steimle et al. 1999), which furthers the possibility of detertion in inferstellar/circumstellar gas.

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## APPENDIX G

FURTHER STUDIES OF 3d TRANSITION METAL CYANIDES: THE PURE ROTATIONAL SPECTRUM OF NiCN ( $\mathrm{X}^{2} \Delta_{\mathrm{i}}$ )
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# Further studies of 3 d transition metal cyanides: The pure rotational spectrum of NICN ( $X^{2} \Delta_{i}$ ) 

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The pure rotational spectum of the NiCN radical $\left(X^{2} \Delta_{i}\right)$ has been recorded using millimeteri sub-mm direct absorption techniques in the range $360-550 \mathrm{GHz}$. Transitions arising from four
 state, as well as lines originating in the $v_{2}$ bending and $v_{1}$ stretching modes. In the vibrational ground state, transitions from both spin-orbit components ( $\Omega=\frac{3}{2}$ and $\frac{3}{2}$ ) were idenified: in the $\Omega=\frac{3}{2}$ ladder, significant lambda-doubling was observed. Multiple vibronic components were found for each bending quantum reconded, a result of Remer-Teller interactions. These components were only observed in the lower spin-orbil ladder ( $\Omega=\frac{3}{2}$ ), however, suggesting that spin-orbit coupling dominates the vibronic effects. The ground-state data were analyzed with a case (a) Hamiltonian, generating rotational, spin-orbit, and lambda-doubling constants for ${ }^{5 l} \mathrm{NiCN}$ and ${ }^{\circ} \mathrm{NiCN}$. The vibrationally excited lines were modeled with effective rotational parameters, except where a case (c) or case (b) coupiing scheme could be meaningfully used. From the ground-state rotational parameters, $r_{0}, r_{s}$, and $r_{\text {wi }}^{(1)}$ structures were derived as well. NiCN appears to be a covaiently bonded molecule with similar properies to NiH. 2003 American Institute of Physics.
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## 1. INTRODUCTION

Molecties containing transition metals bonded to the cyanide moiety are encountered in many aspects of chemical research. For example, nickel-iron cyanide salls such as $\mathrm{K}_{2.8} \mathrm{Ni}_{1.1}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \times 4.5 \mathrm{H}_{2} \mathrm{O}$ have been used in the development of molecule-based ferromagnets with high Curie temperaures.' These materials have potential applications for information storage, color imaging, catalysis, and even bioprocessing. Cyanide-bridged trinuclear complexes containing iron, nickel, copper, and zinc have been investigated for high electrical conductivity, as well as their photophysical propenies. ${ }^{2}$ The absorption of the CN group on transition metal surfaces is also of inierest from aspects of chemisorption mechanisms and toxin removal. ${ }^{3}$ On a more fundamental level, CuCN itself is a known reagent used widely in organic synthesis in the formation of carbon-carbon and siliconcarbon bonds. ${ }^{4-6}$

The interest in transition metal-cyanide compounds has lead theoreticians to compute the structures of some of these species, both as monomers and on surfaces. ${ }^{7,8}$ Boldeyrev, Li. and Wang, ${ }^{9}$ for exmmple, found that CuCN is linear and is more stable than CuNC by $10.7 \mathrm{kcal} / \mathrm{mol}$. In the case of a nickel surface, calculations have shown that the CN group prefers to anach isself to the metal via the carbon atom, therefore producing MCN clusters. ${ }^{7, \%}$ In contrast, known metal-cyanide complexes have either a T-shaped structure, such as NaCN and $\mathrm{KKCN}^{10.11}$ or a linear isocyanide geometry, as in the case of the alkaline-earth metals (MgNC. CaNC ${ }^{12.5}$ ) and aluminum, gallum, and indium. ${ }^{14}$ The tran-

[^7]sition from the T-shaped structure which is very ionic ( $\mathrm{M}^{+} \mathrm{CN}^{-}$), to the isocyanide form occurs as the bonding in the molecule becomes more covalent. ${ }^{15-18}$ The most covalent geometry is predicted to result in the linear MCN form. Until very recently, monomeric metal cyanides have not been experimentally observed.

Because of their intrinsic chemical significance, molecules composed of transition metals bonded to the CN ligand are obvious spectroscopic targets, paricularly the monomeric forms. Surprisingly. liule spectroscopic data exists for these species. The first transition metal cyanide complex invesugated in the gas phase has been $\mathrm{FeNC}\left(K^{*} A_{i}\right) \cdot{ }^{19} \mathrm{LIF}$ spectra were recorded for this radical. which was found to exhibit the linear isocyanide geomery. This study was followed by pure rotational measurements of $\operatorname{CuCN}\left(X^{15}{ }^{+}\right)$ and $\mathrm{ZaCN}\left(X^{2} \Sigma^{+}\right)$, done by the Ziurys group, ${ }^{20.21}$ in which the ground-state structure for both molecules was established to be the linear cyonide form. Recently, Kingsion, Merer, and Varberge ${ }^{32}$ have succeeded in recording a wide range of electronic transitions for NICN, using LIF techniques. These authors found that the linear cyanide geometry is favored energetically for this radical as well. Their work also identified the ground electronic state as ${ }^{2}{ }_{3}$, and determined rotational constants for the $\Omega=\frac{5}{2}$ spin-orbit component. In addition, they observed perturbations in the vibrational structure of NiCN arising from both Fermi resonance and Renner-Teller coupling.

In order to extend our studies of the strucural and bond. ing properies of transixion metal cyanides, we have recorded the pure rotational spectrum of NiCN in its $X^{2} \Delta_{i}$ state. Rotational transitions originating from both spin-orbit componems of the ground state have been observed for the main
isotopomer, ${ }^{5 / W i C N}$, as well as ${ }^{\text {shaCN}}$. In addition, spectra arising from ${ }^{62} \mathrm{NiCN},{ }^{64} \mathrm{NiCN}$, and ${ }^{58} \mathrm{Ni}^{13} \mathrm{CN}$ have been measured. These isotopic substitutions have confimed the linear cyanide structure of NiCN, as established by Kingston et al. Vibrational satellite lines onginating from the first three quanta of the bending mode have additionally been recorded, which exhibit Renner-Teller splimings. Here we present these resules and their spectroscopic analysis, as well as a discussion of structural and bonding trends for transition metal cyanides.

## 13. EXPERIMENT

The pure rotational spectrum of $\mathrm{NiCN}\left(X^{2} \Delta_{i}\right)$ was measured using one of the millimeter/submillimeter wave spectrometers of the Ziurys group, details of which are given elsewhere. ${ }^{23}$ Briefly, the instrument consists of a radiation source, a reaction chamber for molecular synthesis, and a detector. Phase-locked Gunn oscillators and Schottky diode multipliers are used as radiation sources in the frequency range $65-650 \mathrm{GHz}$. Offset ellipsoidal mirrors are employed to propagate the radiation from the source through the reaction chamber, a double-pass system. and to the detector, an InSb bolometer. The reaction cell is water cooled and contains a Broida-type oven. The source is frequency modulated at 25 KHz and detected at $2 f$ using a lock-in amplifier.

The NiCN radical was created by the reaction of nickel vapor, produced in a high-temperature Broida-type oven, with cyanogen gas. Approximately 3-5 mtorr of pure (CN) 2 was introduced into the reaction chamber from undemeath the oven, serving as the carrier gas as well as the precursor. Typical carrier gases such as argon were not found to be necessary. A de discharge was also not needed for the synthesis. While producing NiCN, no chemiluminescence from the reaction was observed. Rotational spectra of all isotopomers were recorded in the natural elemental abundances $\left({ }^{59} \mathrm{Ni}^{60} \mathrm{Ni}^{62} \mathrm{Ni}:{ }^{64}{ }^{\mathrm{Vi}}=68.1: 26.2: 3.6: 0.9\right.$ and ${ }^{12} \mathrm{C}^{13} \mathrm{C}$ $=89.1^{24}$ ).

Final measurements of the rotational transitions were obtained by averaging scans in pairs, with one increasing in frequency and the other in decreasing frequency, each covering a total of 5 MHz . For ${ }^{58} \mathrm{ViCN}$ and ${ }^{60} \mathrm{NiCN}$, one such pair was sufficient: however, the other isotopomers and rotational iransitions originating in excited vibrational states required averages of two to four scan pairs. Typical linewidths ranged from $1000-1300 \mathrm{kHz}$ over the frequency interval $360-550 \mathrm{GHz}$.

## ill. RESULTS

The search for the pure rotational spectrum of NiCN ( $X^{2} A_{i}$ ) was based on the recent optical work of Kingston, Varberg, and Merer. ${ }^{22}$ In their study, rotationally resolved electronic transitions involving the $\Omega=\frac{5}{2} \operatorname{spin}$-orbit component of the ground state ( $v=0$ ) and various vibrationally excited levels were observed for ${ }^{56} \mathrm{NiCN}$ and ${ }^{60} \mathrm{NiCN}$. Hence. estimates of the rotational constants of many vibronic components were available. On the other hand, parameaers for the other spin-orbit level of the ground vibrational state, $\Omega=\frac{2}{2}$, as well as for ouher vibronic states, were not. Conse-
quently a broadband. continuous frequency search $1 \sim 30$ GHz or $>6 \mathrm{~B}$ ) was conducted in an attempt to identify other such sublevels. Because of the presence of Fermi resonance and Renner-Teller interacions, a simple vibrational satellite pattem was not expected as, for example. in the case of ZnCN and $\mathrm{CuCN}{ }^{30.21}$

A further complication arises because the rotational energy levels in NiCN may be split by A-doubling. This interaction, however, is expected to be small in $\Delta$ sutes, as it involves operators to fourth order. ${ }^{25}$ Furthermore, the A-doubling energy term occurs only in off-diagonal marrix elements for the $\Omega=\frac{5}{5}$ componen. whereas for the $\Omega=\frac{\square}{2}$ spin-orbit level there is a direct diagonal contribution. Therefore, the rotational levels of the $\Omega=$ component are expected to exhibit a greater, albeis small. splitting relative to the $\Omega=\frac{\pi}{3}$ sublevel. The optical data of Kingston et al. showed no evidence of $A$-doubling in the $\Omega=$ Fladder: no information whs available for the $\Omega=\frac{1}{2}$ component.

Regular groupings of lines were formunately recognizable at intervals of -2 GHz in frequency space from the ${ }^{38} \mathrm{NiCN}$ ground state $\left(\Omega=\frac{3}{3}\right)$ features. which duplicate themselves in the ${ }^{60} \mathrm{Ni}$ isotopomer. The features steadily decreased in intensity with frequency separation from the ground state. This pattem was assigned to the vibrational satellite progression of the bending mode in the $\Omega=\frac{5}{5}$ component with $U_{2}=1,2$, and 3. The $v_{2}=1$ and 2 sess consist of three and four separate features, respectively-a result of Renner-Teller coupling (see Sec. V). For the $v_{2}=1$ level, the first two lines observed were of equal intensity with a small frequency separation ( $\sim 1 \mathrm{MHz}$ ), while the third was a single feature with a signal strength about a factor of 2 greater. The doublet was assigned to the ${ }^{2} \Pi_{3,2}$ vibronic component and the singiet to the ${ }^{2} \Phi_{7,2}$ sublevel. These assigmments were verified by the optical study. ${ }^{22}$ The strongest fealure for the $v_{2}=2$ set was identified as the ${ }^{2} \Gamma_{9,2}$ vibronic component. as suppored by the optical measurements. The remaining three features were likely to arise from the other two vibronic states. ${ }^{2} \Sigma_{1.2}$ and ${ }^{2} \Delta_{s, 2}$. Because no lambda-doubling was observed for the ground state, $\Omega=\frac{5}{2}$ lines. the ${ }^{2} \lambda_{5 \cdot 2}$ vibronic state transitions should consist of a single feature. The optical study of Kingston et al. ${ }^{22}$ also indicated that this state undergoes Fermi resonance interactions with the $v_{1}=1$ suretch, which also has ${ }^{2} 1_{s / 2}$ symmery. Fermi resonance results in a partial mixing of rotational constants of the two states concemed. and therefore such coupling should shift the ${ }^{2} j_{s, 2}$ vibronic state line to lower frequency relative to the $\Gamma_{92}$ and $\Sigma_{12}$ features. Lines arising from the ${ }^{25} \Sigma_{12}$ state, in contrast. should consist of doublets because of spin-rotation interactions. Consequently, the feature shifted lowest in frequency was assigned to the ${ }^{2} \Delta_{52}$ level, and the remaining two to the ${ }^{2} \Sigma_{12}$ state. The latter two lines, however, must arise from successive N levels, as will be discussed later. ${ }^{26}$ Finally, for the $v_{2}=3$ state, the ${ }^{2} H_{1: / 2}$ and ${ }^{2} \Phi_{7,2}$ vibronic levels were idenvified. The iwo ${ }^{2} \Pi$ substates were not found however. The vibronic sublevels $\Delta_{s_{2}}, \Sigma_{12}, \Phi_{72}\left(v_{2}=3\right)$, and $H_{1 / 2}$, had not been previously observec.

One additional doublet was found approximately 1 GHz higher in frequency from the line arising from the $\Omega=\frac{5}{5}$ sublevel, which was aiso seen in the ${ }^{69} \mathrm{Ni}$ isotopomer. These

Stick Spectrum of NICN $\left(X^{2} A\right): J=54.5-53.5$


FIG. 1. A seick spectrum of the $J=54.5-53.5$ rotarional transixical of ${ }^{53} \mathrm{NiCN}$ and ${ }^{60} \mathrm{NiCN}\left(X^{2} \Delta_{1}\right)$ in the range $464-479 \mathrm{GHz}$ The most imsense line. located nesr 471 GHz arises from the $\Omega=\frac{3}{2} \operatorname{spin}-$-ormit componcos of ${ }^{53} \mathrm{NiCN}$. The $\Lambda$-doublets of the $\Omega=\frac{3}{2}$ subievel lie upproximstely 1 GHz higher in frequency, but are jower in insensiry. The vibrational setelliue progression of the $v_{2}$ bending mode ( $\Omega=\frac{3}{2}$ ) is spaced by shous 2 GHz to higher frequency. Various vitronic components of the $v_{2}=1,2$ and 3 states sree shown, labeled by $\tilde{K}_{F}$. The lines of the ${ }^{2} \Pi_{32}$ level ase split by $P$-type doubling which is caaggerated on this scale. The two spin-sotation components of tie ${ }^{2} \Phi_{\text {siste }}\left(U_{2}=2\right)$ arise from adjacent robational tevels, $N$ $=54-53$ and $55+54$. The $v_{1}=1$ streich lies 60 lower frequency of the ground state lime. A similar patuent is observed for 50 NiCN bus shifted to lower frequency.
features werc assigned to the $\Omega=\frac{1}{2}$ spin-orbit component. split by lambda-doubling. In our past studies of radicals with spin-orbit coupling ( $\mathrm{FeC}, \mathrm{FeF}, \mathrm{FeCl}, \mathrm{CrO}:{ }^{27-31}$ ), rotational lines arising from all $\Omega$ ladders.were found in every case, and NiCN should be no exception. The spin-orbit energy separation for NiCN is certainly comparable. Furthermore, given the spin-orbit spliting of $-830 \mathrm{~cm}^{-3}$ estimated by Kingston et al. ${ }^{22}$ for NiCN, the doublets were not likely to be located far in frequency from the $\Omega=\frac{\sum}{\vdots}$ line, using the approximate relationship, $B_{11}=B(1+2 B \Sigma / A A) .^{32}$ No lines arising from the vibronic states of the $\Omega=\frac{3}{2}$ ladder were observed, however.

Another search was conducted for the first quantum of the heavy-atom stretch, $v_{1}=1$, which lies $501.8 \mathrm{~cm}^{-3}$ above the ground state, comparable in energy to the $v_{2}=2$ level. ${ }^{22}$ Fermi resonance should shif the $v_{1}=1$ feature to somewhat higher frequency, mirsoring the opposite effect in the $v_{2}$ $=2\left(\Delta_{5.2}\right)$ line. A feaure with abous the expecsed intensity was finally found approximately 2 GHz to lower frequency of the ${ }^{58} \mathrm{NiC} \mathrm{N}^{\mathrm{N}}\left(\Omega=\frac{5}{2}, v=0\right)$ line, with a corresponding ${ }^{60} \mathrm{Ni}$ counterpart. These lines were assigned to the $v_{1}=1$ substate, which has ${ }^{2} \Delta_{S / 2}$ vibronic symmetry, as mentioned.

A stick spectrum of the $J=54.5+53.5$ rotational transitions of the ${ }^{38} \mathrm{Ni}$ and ${ }^{60} \mathrm{Ni}$ isotopomers of NiCN near 464 479 GHz is shown in Fig. I, with approximate relative intensities. The strongest feature arises from the $\Omega=\frac{3}{2}$ spinorbit component of ${ }^{58} \mathrm{ViCN}$, as expected. The $\Lambda$-doublets of the $\Omega=\frac{3}{2}$ sublevel are located approximately 1 GHz higher in frequency, labeled $\Delta_{3: 2}$. The remaining lines belong to the
$v_{2}=1,2$, and 3 vibraional progression, whose components are labeled by their vibronic symmery, $\mathcal{K}_{p}$. The ${ }^{2} \Phi_{?, 2}$ and ${ }^{2} \Pi_{3,2}$ states of the $v_{2}=1$ level lie -2 GHz to higher frequency of the $\Omega=\frac{5}{2}$ line: the small P-iype solituing of the ${ }^{2} \mathrm{IH}_{3.2}$ state $(\sim 1 \mathrm{MHz})$ is exaggerated. Approximately 2 GHz to higher frequency from these features are the ${ }^{2} \Gamma_{92},^{2} \Delta_{52}$, and the ${ }^{2} \Sigma_{1.2}$ states. The ${ }^{2} \Sigma^{2}$ level is split by large spinrotation interactions ( $\sim 8 \mathrm{GHz}$ ) such that the two lines shown are from adjacent rotational transitions: in this case $N=54$ -53 and $N=55-54$. The highest-frequency features are the ${ }^{2} H_{1 / 2,}$ and ${ }^{2} \Phi_{1,2}$ vibronic componens of the $\varepsilon_{2}=3$ state. An almost identical pattern of lines is repeated for the 60 NiCN isotopomer, as also shown.

The rotational transition frequencies measured for ${ }^{s 8} \mathrm{NiCN}$ and ${ }^{\text {non }} \mathrm{NiCN}$ in their ground vibrational states are presented in Table I. Over the frequency range 365-535 GHz 19 rotational transitions were recorded for the main isotopomer. ${ }^{58} \mathrm{NiCN}$; for ${ }^{60} \mathrm{NiCN}$, a total of 17 were measured. Both the $\Omega=\frac{5}{2}$ and $\frac{1}{2}$ spin-orbit components were observed in almost every uransition. The latter set consists of $\Lambda$-doublets, with a spliting of approximately 800 MHz . Parity assignments of the $\Lambda$-doublets of the $\Omega=\frac{\vdots}{5}$ sublevel were made based on those for NiH , which has a similar electronic structure. ${ }^{33}$

In Table II, rotational transitions of the ${ }^{62} \mathrm{ViCN},{ }^{5+} \mathrm{ViCN}$. and $\mathrm{Ni}^{13} \mathrm{CN}$ isoopomers $\left(\Omega=\frac{6}{5}\right)$ in their ground vibrational states are presented. Due to their weaker signals. transitions arising from the $\Omega=\frac{2}{5}$ ladder were not observed. Between 14 and 18 lines were measured in the frequency range $360-550$ GHz for each isotopomer.

The data corresponding to the vibrationally excited lines measured for NiCN and its nickel isotopomers. as illustrated in Fig. 1, are complied in three tables available on EPAPS. ${ }^{4}$ As mentioned. rotational rransitions arising from several of the vibronic states of the bending mode were recorded for ${ }^{58} \mathrm{NiCN},{ }^{\text {on }} \mathrm{NiCN}$, and ${ }^{2}{ }^{2} \mathrm{ViCN}$. as well as the first quantum of the heavy atom stretch, $v_{1}=1$, for the ${ }^{58} \mathrm{Vi}$ and thini isotopomers. For both ${ }^{58} \mathrm{NiCN}$ and ${ }^{\text {of }} \mathrm{NiCN}$. spectra arising from the $v_{2}=1\left({ }^{2} \Pi_{3.2},{ }^{2} \Phi_{72}\right), v_{2}=2\left({ }^{2} \Gamma_{9.2},{ }^{3} \sum_{5,2}\right.$, and $\left.{ }^{2} \Sigma_{1,2}\right)$ and $v_{1}=1$ states were measured. For ${ }^{5 n} \mathrm{NiCN}$, transitions in the $v_{2}=3\left({ }^{2} H_{112}\right.$ and $\left.{ }^{2} \Phi_{72}\right)$ level were recorded as well. Finally, measurements of ${ }^{62} \mathrm{NiCN}$ lines originating in the $v_{2}$ $=1\left({ }^{2} \Pi_{3,2}\right.$ and $\left.{ }^{2} \Phi_{7: 2}\right)$ components were made. Between 10-16 rotational transitions were measured in every vibronic state. For the $v_{2}=1:{ }^{2} \Pi_{3 / 2}$ state, $P$-type doublets were recorded for every transition (see EPAPS, Table II), as well as the spin-rotation components in the $\dot{v}_{2}=?: 5_{12}$ state, as shown in EPAPS. Table III.

A representative specturn of boih spin-orbit components of the $J=44.5-43.5$ rotational transition of ${ }^{5} \mathrm{NiCN}$ is shown in Fig. 2. The strongest feature arises from the $\Omega$ $=\frac{3}{2}$ ladder, while the other two weaker lines are the lambdadoublets of the $\Omega=\frac{2}{3} \mathrm{spin}$-orbit component. There are two frequency gaps in this spectrum of about 700 and 800 MHz . respectively, the latter being the approximate separation of

TABLE I. Mensured rotational transitions for NiCN $\left(X^{2} A_{i}\right): v=00^{\circ}$

| $J+1-J$ | $\int 1$ | Pariry | ${ }^{51}{ }^{2} \mathrm{NiCN}$ |  | ${ }^{60} \mathrm{NICN}$ |  | $5+1-j$ | 13 | Paricy | ${ }^{5 \$} \mathrm{NiCN}$ |  | ${ }^{n 0} \mathrm{NiCN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\nu$ sim | $\nu_{\text {abs }}{ }^{-2}$ | $z_{\text {cos }}$ | $y^{\operatorname{cosen}}$ |  |  |  | \#om | $\nu_{\text {cose }}-{ }^{-85}$ | ${ }^{8} 0$ es | pobs - ${ }^{\text {codr }}$ |
| 42.54-41.5 | $5 \Omega$ | $f$ | 367603.305 | -0.059 | 364103.702 | -0.054 |  | $3 / 2$ | 4 | 4 454638.540 | $-0.153$ | \$50 425.926 | -0.149 |
|  | $5 \Omega$ | e | 367603.305 | -0.026 | 364103.702 | -0.025 | 53.5-525 | $5 / 2$ | f | 462415.492 | 0.015 | 458016.081 | 0.032 |
|  | $3 / 2$ | $f$ | 369030.342 | 0.293 |  |  |  | $5 / 2$ | 8 | 462 415.492 | 0.029 | 458018.081 | 0.086 |
|  | $3 / 2$ | e | 368205.169 | 0.064 |  |  |  | $3 / 2$ | $f$ | 464078.605 | -0.132 | + $\$ 9557.056$ | -0.088 |
| 43.5--42.5 | $5 \Omega$ | $f$ | 376230.807 | -0.045 | 372649.261 | $-0.034$ |  | $3 / 2$ | e | 463275.251 | -0.125 | 458983.899 | $-0.062$ |
|  | $5 / 2$ | e | 376230.807 | -0.012 | 372649.261 | -0.005 | 54.5-53.5 | $5 / 2$ | $f$. | 471024.160 | 0.023 | 466543.096 | -0.002 |
|  | 3.2 | $f$ | 377682.521 | 0.076 | 373999.605 | 0.119 |  | $5 / 2$ | $e$ | 471024.160 | 0.033 | 466 543.096 | 0.008 |
|  | $3 / 2$ | e | 376853.552 | 0.144 | 373360.315 | 0.093 |  | $3 / 2$ | $f$ | 472704.482 | -0.206 | 468099.386 | -0.068 |
| 44.5-43.5 | $5 / 2$ | $f$ | 384856.769 | -0.036 | 381193.283 | -0.044 |  | $3 / 2$ | 2 | 471910.668 | -0.087 | 467538.461 | -0.113 |
|  | $5 / 2$ | e | 384856.769 | -0.004 | 381193.283 | -0.015 | 55.5-54.5 | $5 / 2$ | $f$ | 479630.903 | 0.030 | \$75068.241 | -0.016 |
|  | $3 / 2$ | $f$ | 386332.619 | 0.006 | 382565.636 | 0.077 |  | $5 / 2$ | $e$ | 479630.903 | 0.035 | 475068.241 | -0.011 |
|  | $3 / 2$ | e | 385500.888 | 0.860 | 381927.649 | 0.087 |  | $3 / 2$ | $f$ | 481327.788 | -0.151 | 476639.066 | -0.0.48 |
| 45.5-44.5 | 52 | $f$ | 393481.153 | -0.035 | 389735.788 | -0.028 |  | $3 / 2$ | e | 480 54.4.756 | -0.0.8 | 476092.921 | 0.030 |
|  | 52 | e | 393481.153 | -0.003 | 389735.788 | <0.000 | 56.5-55.5 | $5 / 2$ | $f$ | 488235.663 | 0.013 | 483591.5148 | 0.021 |
|  | $3 / 2$ | $f$ | 394980.510 | -0.018 | 391129.489 | 0.043 |  | $5 / 2$ | e | 488235.663 | 0.011 | 483591.514 | 0.021 |
|  | 32 | e | 394147.143 | 0.125 | 390493.932 | 0.069 |  | $3 / 2$ | $f$ | 489948.280 | -0.144 | \$85176.043 | -0.038 |
| 46.5-45.5 | $5 / 2$ | f | 402103.934 | -0.031 | 398276.696 | -0.033 |  | $3 / 2$ | e | 489177.550 | 0.011 | 184645.855 | -0.025 |
|  | $5 / 2$ | e | 402103.934 | $<0.000$ | 398276.696 | -0.005 | 57.5-56.5 | $5 / 2$ | $f$ | 4\%838.450 | 0.017 | 492112.825 | 0.054 |
|  | 3/2 | $f$ | 403626.124 | -0.041 | 399 691,127 | 0.011 |  | $5 / 2$ | 2 | 496838.450 | 0.009 | 492112.825 | 0.049 |
|  | $3 / 2$ | $e$ | 402792.252 | 0.024 | 399059.118 | 0.030 |  | $3 / 2$ | $f$ | 498566.010 | -0.086 | 493710.248 | -0.077 |
| 47.5-46.5 | 512 | $f$ | 410725.072 | -0.029 | 206816.017 | -0.013 |  | 32 | e | \$997808.930 | 0.019 | 293197.456 | -0.0.85 |
|  | 52 | e | 410725.072 | $0.001$ | $406816.017$ | $0.014$ | 58.5--57.5 | $5 / 2$ | $f$ | $505439.190$ | 0.003 | 500632.056 | $0.001$ |
|  | 32 | $f$ | 412269.515 | 0.021 | 408250.523 | $-0.008$ |  | $5 / 2$ | e | 505439.190 | $-0.013$ | 500632.056 | $-0.010$ |
|  | $3 / 2$ | 2 | 411436.320 | 0.004 | 407623.174 | -0.025 |  | $3 / 2$ | $f$ | 507180.950 | 0.045 | 502241.989 | 0.159 |
| $48.5-47.5$ | $5 / 2$ | $f$ | 419344.544 | -0.017 |  |  |  | 32 | $e$ | 506438.920 | 0.017 | 501 247.739 | 0.043 |
|  | $5 / 2$ | e | 419344.544 | 0.012 |  |  | 59.5-58.5 | 52 | $f$ | 514037.870 | -0.006 | 509149.297 | -0.015 |
| 50.5-49.5 | $5 / 2$ | $f$ | 436578.398 | 0.089 |  |  |  | $5 / 2$ | e | 514037.870 | $-0.030$ | 509 149.297 | -0.033 |
|  | $5 / 2$ | 2 | 436578.398 | 0.113 |  |  |  | $3 / 2$ | / | 515792.980 | 0.162 | 510770.764 | 0.161 |
|  | $3 / 2$ | $f$ | 438185.290 | 0.029 |  |  |  | 32 |  | 515067.490 | 0.016 | 510296.594 | 0.208 |
|  | 32 | c | 437361.276 | -0.194 |  |  | 60.5-59.5 | $5 \Omega$ | $r$ | 522634.470 | 0.006 | 517664.494 | $-0.013$ |
| 51.5-50.5 | $5 / 2$ | $f$ | 445192.524 | -0.004 | 440956.514 | 0.091 |  | $5 / 2$ | e | 522634.470 | -0.027 | 517664.994 | -0.038 |
|  | $5 / 2$ | e | 445192.524 | 0.018 | \$40956.514 | 0.110 |  | $3 / 2$ | $f$ | 524 402.120 | 0.302 | 519296.680 | $-0.003$ |
|  | $3 / 2$ | $f$ | 446818.910 | -0.055 | +42464.667 | -0.107 |  | $3 / 2$ | e | 523694.690 | 0.054 |  |  |
|  | $3 / 2$ | e | \$46000.575 | -0.193 | 441867.806 | -0.127 | 61.5-60.5 | $5 / 2$ | $f$ | 531238.877 | -0.041 | 526177.570 | -0.034 |
| 52.5-51.5 | $5 / 2$ | $f$ | 453804.934 | 0.005 | 449487.154 | 0.008 |  | $5 / 2$ | $e$ | 531228.877 | -0.084 | \$26177.570 | -0.068 |
|  | $5 / 2$ | e | 453804.934 | 0.023 | $489487.154$ | $0.025$ |  | $3 / 2$ | ${ }^{e}$ | 532320.300 | 0.201 |  |  |
|  | 32 | $f$ | 459450.069 | $-0.073$ | \$51012.114 | -0.119 |  |  |  |  |  |  |  |

${ }^{2} \ln \mathrm{MHz}$.
the $\Omega=\frac{1}{2}$ lambda doublets. The relative intensities of these spin-orbit components are consistent with their energy separation of $-830 \mathrm{~cm}^{-1} .22$

Figure 3 presents a spectram of the $\Omega=\frac{2}{2}$ spin-orbit components of the $J=43.5-42.5$ transition for the ${ }^{56} \mathrm{NiCN}$ and ${ }^{58} \mathrm{Ni}^{13} \mathrm{CN}$ isotopomers. The line corresponding 10 ${ }^{58} \mathrm{Ni}^{13} \mathrm{CN}$ is quite weak relative to the main isotopomer, and therefore this section of the spectrum is shown as an inset. The relative intensities of these lines are consistent with the ${ }^{12} \mathrm{C} /{ }^{13} \mathrm{C}$ natural abundance ratio of $-90 .{ }^{24}$

## IV. ANALYSIS

The rotational spectra for the ground vibrational suate of NiCN were analyzed using the following effective Hamiltonian, ${ }^{25,3536}$

$$
\begin{equation*}
\hat{H}_{\mathrm{eff}}=\hat{H}_{\mathrm{ROT}}+\hat{H}_{\mathrm{SO}}+\hat{H}_{\mathrm{LD}} \tag{1}
\end{equation*}
$$

where the three terms concern the molecular frame rotation. spin-orbit coupling, and lambda-doubling. The form of the spin-orbir Hamiltonian can be found in Ref. 35, which in-
cludes its centrifugal distortion corrections. The lambdadoubling Hamilionian involves the constants $\bar{q}_{3}$ and $\tilde{p}_{3}$. as defined in a case (a) basis, ${ }^{25}$ as well as several higher-order cenurifugal distomion terms.

$$
\begin{equation*}
\hat{H}_{\mathrm{LD}}=\hat{H}_{\mathrm{LD}}^{\prime}+\hat{H}_{\mathrm{LD}}^{\prime \prime} \tag{2}
\end{equation*}
$$

where

$$
\begin{equation*}
\hat{H}_{\mathrm{LD}}^{\prime}=1 / 2 \tilde{q}_{\Delta}\left(J_{+}^{4}+f_{-}^{4}\right)-1 / 2 \tilde{p}_{د}\left(J_{-}^{3} S_{-}+J_{-}^{3} S_{-}\right) \tag{3}
\end{equation*}
$$

and

$$
\begin{align*}
\hat{H}_{L D}^{\prime \prime}= & -1 / 4 \bar{p}_{\Delta D}\left[\left(J_{-}^{3} S_{+}+J_{-}^{3} S_{-}\right) \cdot \mathbb{R}^{i}\right] \\
& -1 / 4 \tilde{p}_{\Delta H}\left[\left(J_{+}^{3} S_{+}+J_{-}^{3} S_{-}\right) \cdot R^{3}\right]_{-} \\
& -1 / 4 \tilde{p}_{\Delta L}\left[\left(J_{+}^{3} S_{+}+J_{-}^{3} S_{-}\right) \cdot R^{6}\right] \\
& -1 / 4 \tilde{p}_{\Delta p}\left[\left(J_{+}^{3} S_{-}+J_{-}^{3} S_{-}\right) \cdot R^{\overline{4}}\right]_{-} \tag{4}
\end{align*}
$$

The quantum number $R$ here describes the rotational angular momentum, where the total angular momentum is defined as $\hat{\tilde{J}}=\hat{\mathbf{R}}+\hat{\mathbf{L}}+\hat{\mathbf{S}}$.


| $y \div 1-1$ | ${ }^{4} \mathrm{NaCN}$ |  | ${ }^{3} \mathrm{NiCN}$ |  | ${ }^{59} \mathrm{Ni}^{13} \mathrm{CN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Vobs | $\gamma_{\text {cose }}{ }^{-1}$ | $\mathrm{Hs}_{\text {dem }}$ | Prose $V_{\text {cade }}$ | Fots | $v_{\text {stas }}-V_{\text {cald }}$ |
| 42.5-48.5 |  |  |  |  | 364062.363 | -0.021 |
| 43.5-42.5 | 369289.849 | -0.049 | 366132.736 | 0.0097 | 372606.776 | -0.015 |
| 4.4.5-4.4.5 | 377757.081 | -0.005 | 374527.702 | 0.004 | 381149.701 | 0.022 |
| 45.5-44.5 | 386222.737 | -0.021 | 382921.121 | -0.053 | 389691.059 | 0.004 |
| 46.5-\$5.5 | 394688.898 | 0.018 | 391313.115 | -0.011 | 398230.734 | -0.028 |
| 47.5-46.5 | 403189390 | -0.028 | 309703.455 | -0.064 |  |  |
| 48.5-47.5 | $411610.34 \%$ | 0.003 | 408092.355 | 0.035 |  |  |
| 51.5-50.5 |  |  |  |  | 490904.381 | -0.067 |
| 52.5-51.5 | 4.9597.186 | 0.033 |  |  | 449433.953 | 0.022 |
| 53.5-52.5 | 453889.522 | 0.051 | 450011.270 | $<0.000$ | 457961.578 | -0.003 |
| 54.5-53.5 | 462339.994 | 0.028 | 458389.792 | -0.022 | 466487.422 | 0.058 |
| 55.5-54.5 | 470788.615 | 0.011 | 466766.599 | 0.067 | 475011.270 | 0.026 |
| 56.5-55.5 | 479235.290 | -0.062 | 475141.491 | 0.102 | 483533.187 | $<0.090$ |
| 57.5-56.5 | 487680.226 | 0.052 | 483 314.408 | 0.053 | 492053.191 | 0.034 |
| 58.5-57.5 | \$96123.121 | 0.083 |  |  | 500571.088 | -0.032 |
| 59.5-58.5 | 504563.882 | -0.027 | 500254.435 | -0.030 | 509087.043 | 0.002 |
| 60.5-59.5 | 513002.685 | -0.068 | 508621.579 | 0.037 | 517600.825 | -0.060 |
| 61.5-60.5 | 521439.548 | 0.012 | 516986.473 | -0.127 | 526112.627 | 0.011 |
| 62.5-61.5 | 529874.186 | -0.032 |  |  | 53.422 .130 | -0.071 |
| 63.50-62.5 |  |  |  |  | 543129.680 | 0.077 |

The ${ }^{5 R^{2}} \mathbf{N i C N}$ and ${ }^{69_{N J C N}}$ data sets were separately analyzed using this Hamilonian in a nonlinear least squares fitiong routine. In both cases, the spin-orbit coupling con$\operatorname{stan} A$ was fixed to the value of -12441000 MHz . ${ }^{22}$ Four centrifugal correction serms to the lambda-doubling term $\tilde{p}_{A}$ were found necessary for both analyses. (Centrifugal distortion corrections to $\tilde{q}_{\Delta}$ were found not to improve the rms of the fit.) Such higher-order terms are not unusual for lambdadoubling in states where $\Omega>1$. In the $X^{3} \Phi$ state of CoH, for example. $q_{D}, q_{H}$ and $q_{L}$ were necessary to fit the optical spectrum. ${ }^{37}$ For the remaining isotopomers ${ }^{62} \mathrm{NiCN},{ }^{64} \mathrm{NiCN}$, and ${ }^{5 R} \mathrm{Ni}^{13} \mathrm{CN}$, rotational parameters for the $\Omega=\frac{5}{3}$ spin-orbit level were determined.

The resulting spectroscopic constants for the isotopomers of NiCN in its ground vibrational state are presented in Table III. As shown in the table, all parameters are well determined, even the higher-order terms. and the rns of each fit is $<99 \mathrm{kHz}$-below the estimated experimental error of $\pm 100 \mathrm{kHz}$. Also given in the table are rotacional parameters obtained from Kingsion et a!.$^{22}$ for ${ }^{5}{ }^{8} \mathrm{ViC}, \mathrm{N}$ and ${ }^{69} \mathrm{ViCN}$ for the $\Omega=\frac{5}{2}$ ladder. The millimeter-wave and optical constants are in good agreement.
 was fit separately. For the $v_{2}=1$ vibronic levels ( ${ }^{2} \Pi_{32}$ and ${ }^{2} \Phi_{12}$ ), the transitions were analyzed using the following case (c) energy level expression:2 ${ }^{2,38}$

TABLE III. Spectoscopic paramesers of NiCN $\left(R^{-3} A_{1}\right): v=0^{8}$

| Parameter | Millinter-wave |  |  |  |  | Optical ${ }^{\text {a }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ${ }^{51} \mathrm{NiCN}$ | ${ }^{6} \mathbf{2} \mathbf{N i C N}$ | ${ }^{62} \mathrm{NiCN}$ | ${ }^{6} \mathrm{NiCN}$ | ${ }^{51} \mathrm{Ni}^{13} \mathrm{CN}$ | S ${ }^{\text {WhCN }}$ | finsic. |
| 8 | 4336.1484617) | 4294.8378(14) |  |  |  |  |  |
| D | $0.00150386(28)$ | $0.00147643(24)$ | * |  |  |  |  |
| $B_{\mathbb{G}= \pm 1}$ | 4330.05691161 | 4288.7898(17) | 4250.0835117) | 4213.70761181 | 4288.34161161. | 4330.00-4901 | 4258.8461126) |
| $D_{0 \times 5 / 2}$ | 0.00147034271 | $0.00144398(28)$ | $0.00141948(27)$ | 0.001396581301 | 0.001454 59(25) | 0.0015018 ; | 0.00: 53121 |
| $A$ | -1241000\% | -12441000\% |  |  |  |  |  |
| Ao | -5.3381117) | -5.3109 1141 |  |  |  |  |  |
| $A_{H}$ | 0.000032151291 | $0.00003112(24)$ |  |  |  |  |  |
| $\bar{p}$ | $0.4090(87)$ | 0.347111) |  |  |  |  |  |
| $\hat{P}^{\text {a }}$ | -0.0001406(77) | -0.000 1319194] |  |  |  |  |  |
| $\bar{p}_{3 H}$ | $3.20130) \times 10^{-5}$ | $3.07(37) \times 10^{-1}$ |  |  |  |  |  |
| $\bar{p}_{3 L}$ | $-4.19(56) \times 10^{-12}$ | $-4.28(69) \times 10^{-12}$ |  |  |  |  |  |
| $p_{s P}$ | $23.34(41) \times 10^{-16}$ | $2.55(50) \times 10^{-36}$ |  |  |  |  |  |
| $\mathrm{a}_{3}$ | 0.0000833 (76) | $0.0000741(70)$ |  |  |  |  |  |
| 52085 | 0.099 | 0.075 | 0.041 | 0.057 | 0.041 |  |  |

[^8]

FhG. 2. A representasive spectram of ${ }^{58} \mathrm{NiCN}\left(X^{2} A_{i}\right)$ showing bath the © $=\frac{3}{2}$ and $\Omega=\frac{3}{2}$ spin-orbin components of the $J=44.5+43.5$ rosasional aransition near 385 GHz Two frequency gaps of -700 MHz tach are present in this specorum. The $\Omega=\frac{3}{2}$ feature is more intense, consistent widh the imverued ground electrous stase. The $1=\frac{3}{2}$ spin-orbit component is split into two lines with similar intensities by lambda-doubling. This specornum is a composite of three 100 MHz scants. each -1 min in duration

$$
\begin{align*}
F_{\mathrm{rot}}= & B J(J+1)-D J^{2}(J+1)^{2}+H J^{3}(J+1)^{3} \\
& \pm q / 2(J-1 / 2)(J+1 / 2)(J+3 / 2) . \tag{S}
\end{align*}
$$

The last term in this equation describes $P$-type doubling, which was only needed for the ${ }^{2} \Pi_{3,2}$ vibronic state. Spinrotation coupling had to be considered for the ${ }^{2} 5$ vibronic level. which was consequently fit using the standard case (b) Hamiltonian in integer quantities of $N$. As mentioned, the two-spin-rotation componens per transition ( $N+1-N$ ) were separated by almost $2 B$. Such large spin-rotation parameters are commonly present in ${ }^{2} \Sigma$ vibronic states. ${ }^{39}$ The


FIG. 3. A spectrum stowing the $\Omega=\frac{5}{2}$ spin-orbis components of the $J$ $=43.5-42.5$ roistionel unansition of ${ }^{58} \mathrm{NiCN}$ and ${ }^{58} \mathrm{Ni}^{13} \mathrm{CN}$, measured neap 376 GHz in the natural shoundence of carboa. Exch section is approximately 30 MHz in width with a frequemcy gap of about 3.5 GHz . The ${ }^{s h} \mathrm{Ni}^{13} \mathrm{CN}$ cature is 800 weak so be obseryed on the same scale as shNiCN. Thus, an enlarged siew is shown in the inset, which consists of an average of forr, 5 MHz scens, each with a duration of about 30 s . The main spectruma is composed of data taken from two, 100 MHz scans, each lasting -1 min.
remaining vibronic components of the $t_{2}=2$ and 3 levels were analyzed with effective rotational constants. The results of these analyses are given in Table IV. along with rotational parameters derived from the optical studics, when available. Again, here is excellent agreement between the data sets.

## Y. DISCUSSION

## A. The structure of NiCN

Because a sufficient number of isotopomers of NiCN have been studied, several structures can be obtained for this molecule. Unfortunately, both spin-orbit components were observed for only the ${ }^{\mathrm{SNiCN}} \mathrm{Nand}$ NiCN species. Therefore, only an $r_{0}$ geomerry can be calculaied for this molecule based on the rotational constants in the ' $\$$, ground state. The resulting bond lengths are $r_{\mathrm{xi}}=1.8281(6) \mathrm{A}$ and $r_{\mathrm{CN}}$ $=1.1580(8) A$, as shown in Table V. However, rotational spectra of five sotopomers in the $\Omega=$ ladder were measured: thus, $r_{0} / r_{s}$, and $r_{m}^{(1)}$ structures based on these data can also be derived. The $r_{0}$ geomerries were established by doing a nonlinear least-squares fit to the moments of inertin for the specific isotopomers, while the $r$, structure was derived using Kraitchman's equations. ${ }^{\text {n }}$ The $r_{m}^{!1]}$ geomerry was determined using the method of Watson. ${ }^{-1}$ which partially corrects for zero-point vibrations. The calculation of an $r_{m}^{(2)}$ structure could not be done because the nitrogen atom was not isotopically substituted.) These geometries are presented in Table $V$. As shown. the resulting bond lengths agree to within $0.003 \AA$ for the Ni-C bond. the shonest value ( 1.8263 $\AA$ ) being that obtained by the $r_{m}^{t 1)}$ method. The $\mathrm{C}-\mathrm{N}$ bond distances vary by only 0.007 A : again. the shortest bond length is the $r_{m}^{(1)}$ value $\left(r_{\mathrm{C}}=1.152 \mathrm{~A}\right)$. The $r_{0}(\Omega=5)$ structure also agrees with that obtained by Kingston et al. to within $0.0001 \AA$ : their values were derived from the ${ }^{j \pi} \mathrm{NiCN}$ and ${ }^{58}{ }^{3} \mathrm{ViC}^{15} \mathrm{~N}$ isotopomers only.

Also included in Table $V$ are the structures for CuCN , ZnCN , and GaCN . For gallium. the more stable isomer is actually GaNC, but for comparison the cyanide is more appropriate.) From nickel through gallium. the metal-carbon bond length steadily increases. although not uniformly. For example, the $\mathrm{Cu}-\mathrm{C}$ and $\mathrm{Ni}-\mathrm{C}$ bond lengths are quite similar. differing by only $-0.01 \AA$. This result is expected because the electronic configurations differ by only one nonbonding $\delta$ electron. The metal-carbon bond lengths for these iwo molecules thus reflect their aromic radi. ${ }^{\text {it }}$ In contrast. the $\mathrm{M}-\mathrm{C}$ bond length difference between CuCN and ZnCN is significantly larger, in fact, nearly 0.11 A. As suggested by ob initio calculations, ${ }^{9}$ the change in configuration from CuCN to ZnCN involves the addition of an exura electron into an antibonding $5 \sigma$ molecular orbital. Hence. the lengthening of the metal-carbon bond is expected. Similarly, an increase of $\sim 0.11 \AA$ is observed between the $\mathrm{Zn}-\mathrm{C}$ and $\mathrm{Ga}-\mathrm{C}$ bond lengths, which can be explained by the addition of a second electron into this $5 \sigma$ orbital. There is limle difference between most of the $\mathrm{C}-\mathrm{N}$ bond lengths, which are very close to that in $\mathrm{HCN}\left(r_{e}=1.1532 \AA\right) .^{+3}$ The exception here is ZnCN , which has $r_{C N}=1.1417 \AA$. anomalously shon, ${ }^{2}$ "

The relative strengths of the metal-carbon bond can be estimated from the corresponding stretching tesuencies. The

TABLE [V. Spectroscopic paramelers for vibronic states of NICN $\left.\left(\mathrm{N}^{-2} y_{i}\right)\right)^{2}$

${ }^{4}$ Is MHz eroors are 30 and apply wo the last quoted decimai places.
${ }^{3}$ From Ref. 22. Values are originally quoted in $\mathrm{cm}^{-1}$.
Fit with a case (b) Hamitonian with integer quantum numbers.
frequency of the $\mathrm{Ni}-\mathrm{C}$ stresch, $\omega_{1}$, has been measured by Kingston et al. to be $501.8 \mathrm{~cm}^{-1} .22$ As an independent test. $\omega_{1}$ can also be approximated using the Kratzer reiationship, ${ }^{\text {th }}$ if the C: ligand is treared as a unis. For ${ }^{58} \mathrm{NiCN}, \omega_{1}$ was calculated to be $491 \mathrm{~cm}^{-1}$. The value computed for CuCN, using the same assumptions, was 478 $\mathrm{cm}^{-1} .{ }^{20}$ These stretching frequencies are much larger than those estimated for ZnCN and GaCN , which are 418 and 348 $\mathrm{cm}^{-1},{ }^{1+31}$ respectively. This comparison implies that the metai-carbon bond in NiCN , a free radical. is similar to that of CuCN, a closed-shell molecule. The extra electron in the diffuse $\delta$ nonbonding molecular orbital in CuCN does not apparently influence the metal-carbon bond io any significant degree.

Rotational transitions within the first three quanta of the bending mode were observed: consequently, the vibrationrotation constanh, $\alpha_{2}$, can be estimated for NiCN , using the expression $B_{\mathrm{v}}=\tilde{B}_{c}-\alpha_{2}\left(\nu_{2}+1\right)$, where $\bar{B}_{c}=B_{e}-1 / 2\left(\alpha_{1}\right.$ $\left.+a_{3}\right)$. Using the values of $\left.B_{10}=s, 2\right)$ for the ${ }^{2} \Delta_{5,2},{ }^{2} \Phi_{7: 2}$, ${ }^{2} \Gamma_{9.2}$, and ${ }^{2} H_{1 / 2}$ states $\left(v_{2}=0,1,2\right.$, and 3 ), a least-squares analysis results in $\bar{B}_{4}=4307.4626(12) \mathrm{MHz}$ and $\alpha_{2}$ $=-22.3746(5) \mathrm{MHz}$. The value obtained for $\alpha_{2}$ is consistent with those calculated for CuCN and ZnCN , which are $-26.7125(4) \mathrm{MHz}$ and -31.597416$) \mathrm{MHz}$, respectively. ${ }^{20.21}$

Hence. $\alpha_{2}$ scales approximately with mass for all threc species. indicauing these metal cyanides are fairly riyid and not subject to quasilinear behavior.

## 8. Renner-Teller interactions in NiCN

The pure rotational specua measured here clearly indicate that for NiCN. the spin-orbit splitung is significantly larger than the Renner-Teller coupling, i.e.. $A>\varepsilon \omega$. The Renner parameter $\varepsilon$ is really defined only for $\Pi$ states. ${ }^{39,45.46}$ ) The identification of almost all Renner-Teller componenes for the three quanta of the bend originating from the $\Omega=\frac{5}{5}$ ladder, but none in the other spin-orbit component ( $\Omega$ $=\frac{3}{2}$ ), is good evidence for this extreme case. In the romational spectra, the spliting between the vibronic components is small. as well. indicating weak Renner-Teller coupling. These findings are in agreement with the optical study of NiCN .

An energy level diagram illustrating the relative contributions of Renner-Teller and spin-orbir couplings is presented in Fig. 4. Only levels for $v_{2}=1,2$, and 3 are shown for simplicity. Detecied levels are indicated by solid lines and those not observed by dashed lines. As shown. RennerTeller coupling effecively generates "duplicate" vibronic


FIG. 4. An energy level diagram of the vibratiomal manifold for NiCN. The vibronic components of the first three quanta of the bending mode, which are gencrated by Remer-Teller interactions, are shown in both spin-orbat components. The separation of the two spin-ortit ladders is roughly 830 $\mathrm{cm}^{-1}$, zs indicated. The solid lines represeral vitronic levels measured in this wouk while the dashed ones were not observed The ${ }^{2} y_{s_{2}}$ vibronic level of the $z_{2}=2$ mode is shifted in energy by Fermi resonance. as indicased by the (xrow. As shown only the vibrenic components of $\Omega=\frac{5}{2}$ were observed in this work, indicating that the spin-orbit interactions are greater than Remer-Teller couplings. The approximate energies of the vibronic components are largety based on the work of Kingston et al.)
however, as described by Peric and Peverimhoff. ${ }^{\text {n }}$ Using expressions from these authors for the case where $A>a \omega_{2}$, $c \omega_{2}$ ( $\omega_{2}$ is the bending frequency), $c$ and $u$ can be calculated from the energies measured for the $v_{2}=1, \Phi_{7.2}$, and $\Pi_{32}$ vibronic levels from Kingston at al. 1244.9641 and 243.6398 $\mathrm{cm}^{-1}$, respecively). The values determined are $c=0.0333$ and $a=0.00228$, which yield $E(2 \Sigma)=476.5 \mathrm{~cm}^{-1}, E\left(^{2} \Delta\right)$ $=475.9 \mathrm{~cm}^{-1}$, and $E\left({ }^{2} T\right)=485.4 \mathrm{~cm}^{-1}$. The energy for the $\Gamma$ state compares well with that deduced from the dispersed fluorescence spectra of NiCN, which is $-475 \mathrm{~cm}^{-1}{ }^{22} \mathrm{As}$ these numbers show, Renner-Teller coupling in NiCN does not significantly separate the $v_{2}=2$ vibronic leveis. Any additional shifting of energies must be a result of Fermi resonance.

## C. Lambda-doubling in NICN

The theory of lambda-doubling has been studied in some detail for $\Delta$ elecronic states, where it requires a treament by fourth-order perturbation theory- ${ }^{25}$ In general. this interaction
is not expected to be as large as in $\Pi$ states. Nonetheless, lambda-doubling has been observed in ${ }^{3} A, S^{5}$, and ${ }^{n} A$ states. ${ }^{29.30 .51 .52}$

In ${ }^{2} \Delta$ states, lambda-doubling has been investigated, io our knowledge, in only two molecules: WiH ${ }^{33,53}$ and NiCN . Lambda-doubling was observed in both spin-orbit components for the hydride, in contrast to the cyanide. In NiH, the splitting in the $\Omega=\frac{2}{2}$ ladder was quite large, in fach on the order of many gigaherrz in the lower rotational levels, corresponding to $\tilde{p}_{\perp}=188.614 \mathrm{MHz}$. In NiCN , the $\bar{p}_{3}$ parameter is much smaller. 0.4090 MHz , which generates splittings of the order 800 MHz in the transitions studied here. The $\bar{q}_{\Delta}$ constants also vary by several orders of magnitude between the two molecules. The large difference in lambda-doubling parameters between NiH and NiCN is expected since this interaction is mass dependent.

Lambda-doubling constants can be used to obtain information about the excited electronic states, which perturb the ground state and give rise to this phenomenon. If one assumes that the splitting arises from perturbations of unique I and II excited states (i.e., the "pure precession" model), then the lambda-doubling $p_{A}$ constant can be related to the energy differences between these states via the following expression: ${ }^{23.52}$

$$
\begin{equation*}
p_{د}=\frac{96 B^{3} A}{\left(E_{1}-E_{\square}\right)^{2}\left(E_{\Delta}-E_{\mathbf{S}}\right)} \tag{6}
\end{equation*}
$$

Here $B$ is the rotational constant of the ground state, $A$ is the spin-orbit parameter, and $E_{\Sigma}$ and $E_{\eta}$ are the energies of the closest perturbing excited ${ }^{2} \Sigma$ and ${ }^{2} \Pi$ states, respectively. The constant $p_{3}$, derived in a case (b) basis, can be related to $\tilde{\rho}_{\Delta}$ and $\tilde{q}_{\Delta}$ via the relationship $\rho_{\Delta}=\bar{\rho}_{A}-4 \tilde{q}_{3} .{ }^{29}$

For NiCN , the energy of the nearest ${ }^{2} \Sigma$ state has not yet been measured. The lowest-lying $\Delta_{3: 2}$ state has been observed optically and $E_{\mathrm{B}_{32}}-E_{\mathrm{n}_{39}}=1408 \mathrm{~cm}^{-1} .^{22}$ ) Assuming that $\tilde{p}_{\Delta} \sim \rho_{\Delta}$ (i.e., $\tilde{q}_{\Delta}$ is negligible), the ${ }^{2} \Delta_{32}-{ }^{2} \Sigma$ energy difference for NiCN can be calculated using Eq. 16). (We use the ${ }^{2} \Delta_{3.2}$ spin-orbit component because this sublevel alone was used to derive $\bar{p}_{\Delta}$.) This energy was calculated to be $\Delta E-4.5 \mathrm{~cm}^{-1}$, suggesting that there is a low-lying excited ${ }^{2} \Sigma$ state in the vicinity of the $\Omega=\frac{3}{\vdots}$ ground state spin-orbit component.

This approximation, however, is an oversimplification. As described by Kingston es al, there are many low-lying excited electronic states, so the notion of "unique perturbers" cannot be accurate. Moreover, there is thought to be significant mixing of the ${ }^{3} \Delta_{3,2}$ sub-state with a nearby ${ }^{2} \mathrm{H}_{3,2}$ state. Perhaps a "supermultiplet" model is more appropriate for NiCN . as has been used to describe $\mathrm{NiH} .{ }^{54}$ On the other hand, applying the same expression to NiH , where the energy differences of nearby $\Sigma$ and $\Delta$ excited states have been measured. ${ }^{33.52}$ a calculation of the $p_{3}$ parameter yields 227 MHz . This value is in relatively good agreement with the measured number, $p_{\mathrm{A}}=190 \mathrm{MHz}$.

## D. Evidence for covalent bonding

Another interesting question concerning NiCN is the nature of the nickel-cyanide bond. Although the cyanide moi-
ety can exist as $\mathrm{CN}^{-}$, as is found in NaCN and $\mathrm{KCN},{ }^{10.11}$ there is evidence that the $\mathrm{Ni}^{-} \mathrm{CN}^{-}$contiguration is not parsiculariy significant for this molecule. The electronic ground state of NiCN is ${ }^{2} 1$, for example, which is the same as for NiH. Given the small elecironegaivity difference between nickel and hydrogen ( 0.029 ), the bonding is likely to be quite covalent in the hydride. In connast two ionic nickel-bearing compounds, NiF and NiCl , both have ${ }^{2} \Pi$ ground electronic states. ${ }^{55,36}$ The electronegativiny difference between nickel and fluorine is 2.07 -an order of magnitude larger than in NiH . It can thus be inferred that the metal-ligand bond in NiCN resembles NiH more closely than the ionic species NiF and NiCl . arguing for a significant covalent character in this molecule.

Additional evidence for covalent bonding in NiCN arises from the spin-orbit constant. Using the energy levels of the ${ }^{2} \mathrm{D}$ ground state of $\mathrm{Ni}^{+},{ }^{57}$ the spin-orbit constant is calculated to be $-603 / 8 \mathrm{~cm}^{-1}$. The spin-orbit constant of NiCN is $-415 \mathrm{~cm}^{-1}$, significandy lower than that of the $\mathrm{Ni}^{-}$. In fact. it is closer to the value for a nickel atom: $-330 \mathrm{~cm}^{-1} .57$ Hence, in NiCN, the nickel behaves more like the neutral atom than the ion, again supporing a covalent picture of the Ni -ligand bond.

Perhaps the best argument for covalency arises from the linear cyanide structure of NiC. itself. This geometry, which is also observed in the zine and copper analogs. ${ }^{20.21}$ can be explained by considering the metal aomic orbitals involved in bonding. The $\mathrm{Ni}-\mathrm{C}$ bond occurs through a $\sigma$-type molecular orbital formed from the metal $4 s$ orbital and $5 \sigma$ molecular orbital of CN . The $\overline{5} \sigma$ orbital has slighly more nitrogen character, and. hence. at first glance. the metal should bond to the N atom. However, nickel also possesses a nearly full $3 d$-electron subshell. $3 d^{\S}$. The $3 d$ subshell is still relatively close in energy to both the 4 s level for this atom and the unoccupied $\pi$ antibonding molecular orbital of CN , which is more carbon in character. Thus. nickel $3 d$ electron density can back-bond into the empty -7 molecular orbitals of CN, which consequently results in the preference of a $\mathrm{Ni}-\mathrm{C}$ bond. The presence of back-bonding is usually associnted with covalent bonding as well.

## V. CONCLUSION

Measurement of the pure rotational spectrum of NiCN in its ${ }^{2} \$_{i}$ ground electronic state has enabled the identification of both spin-orbit componens of this molecule. as well as new vibronic levels. It has also confirmed the linear cyanide structure of this radical, as indicated by optical studies. In the higher lying spin-orbit sublevei ( $\Omega=\frac{2}{5}$ ), significant lambdadoubling interactions were observed. as has also been found in NiH $\left(X^{2} د_{i}\right)$. These fincings suggest a low-lying excited ${ }^{2} \Sigma$ state. Several quanta of the $v_{2}$ bending mode were observed in the data, which follow a regular pattem and suggest that NiCN is a fairly rigid species. even though it is a radical. Many vibronic components of the $\tau_{2}$ bend were also idenijfied but only those arising from the lower spin-orbit component, $\Omega=\frac{\text {. }}{}$. Renner-Teller coupling is therefore considerably smaller relative to the spin-orbit spliting. Among vibronic levels investigated was the ${ }^{5} \Sigma_{12}\left(c_{2}=2\right)$ substate.
which exhibits large spin-rotation spliting ( $\gamma \sim 2 B$ ) due to spin-uncoupling effects. The linear cyanide structure for NiCN, the value of iss spin-orbit constant and its ground electronic state all indicate that the bonding in this radical is predominantly covalent.

## ACKNOWLEDGMENTS

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EPAPS Table I. Measured Rotational Transitions of Vibronic States of NiCN $\left(\mathrm{X}^{2} \Delta_{i}\right)^{2)}$

| $\left(\mathrm{v}_{1}, \mathrm{v}_{2}, \mathrm{v}_{3}\right) \mathrm{K}_{\mathrm{P}}$ | $\mathrm{J}+1 \leqslant \mathrm{~J}$ | ${ }^{38} \mathrm{NiCN}$ |  | ${ }^{69} \mathrm{NiCN}$ |  | ${ }^{62} \mathrm{NiCN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\nu_{\text {cba }}$ | $\nu_{\text {obs }}-V_{\text {calc }}$ | $\nu_{\text {diss }}$ | ${ }^{\text {obs }}$ - $V_{\text {calc }}$ | $\nu_{\text {coss }}$ | $\nu_{\text {obs }}-\nu_{\text {casc }}$ |
| (010) $\Phi_{7 / 2}$ | $42.5 \leftarrow 41.5$ | 369511.212 | 0.011 | 365990.942 | 0.026 |  |  |
|  | $43.5 \leftarrow 42.5$ | 378185.355 | 0.013 | 374582.552 | 0.008 | 371203.304 | -0.028 |
|  | $44.5 \leftarrow 43.5$ | 386858.016 | -0.017 | 383172.723 | -0.024 | 379716.218 | 0.052 |
|  | $45.5 \leftarrow 44.5$ | 395529.236 | $<0.000$ | 391761.493 | 0.007 | 388227.536 | -0.024 |
|  | $46.5 \leftarrow 45.5$ | 404198.908 | -0.005 | 400348.698 | -0.029 | 396737.445 | -0.034 |
|  | $47.5 \leftarrow 46.5$ |  |  |  |  | 405245.904 | 0.019 |
|  | $50.5 \leftarrow 49.5$ | 438861.590 | 0.002 | - |  |  |  |
|  | $51.5 \leftarrow 50.5$ | 447523.043 | -0.010 | 443261.100 | -0.010 | 439263.654 | 0.013 |
|  | $52.5 \leftarrow 51.5$ | 456182.744 | -0.013 | 451838.555 | $<0.000$ | 447763.932 | 0.008 |
|  | $53.5 \leftarrow 52.5$ | 464840.659 | $<0.000$ | 460414.249 | 0.017 |  |  |
|  | $54.5 \leftarrow 53.5$ | 473496.724 | 0.004 | 468988.099 | -0.002 | 464759.240 | 0.004 |
|  | $55.5 \leftarrow 54.5$ | 482150.897 | -0.001 | 477560.134 | 0.013 | 473254.201 | 0.014 |
|  | $56.5 \leftarrow 55.5$ | 490803.130 | -0.022 | 486130.263 | 0.009 | 481747.337 | 0.056 |
|  | $57.5 \leftarrow 56.5$ | 499453.430 | -0.009 | 494698.469 | 0.011 | 490238.357 | -0.123 |
|  | $58.5 \leftarrow 57.5$ | 508101.828 | 0.110 | 503264.667 | -0.025 | 498727.802 | 0.059 |
|  | $59.5 \leftarrow 58.5$ | 516747.918 | -0.029 |  |  | 507215.121 | 0.091 |
|  | $60.5 \leftarrow 59.5$ | 525392.046 | -0.035 |  |  |  |  |
|  | $61.5 \leftarrow 60.5$ |  |  |  |  | $524183.541$ | $0.030$ |
|  | $62.5 \leftarrow 61.5$ |  |  |  |  |  | 0.055 |
| (020) $\Delta_{s / 2}$ | $51.5 \leftarrow 50.5$ | 449192.863 | 0.037 | 444853.305 | 0.086 |  |  |
|  | $52.5 \leftarrow 51.5$ | 457865.234 | -0.036 | 453442.336 | -0.031 |  |  |
|  | $53.5 \leftarrow 52.5$ | 466535.064 | -0.001 | 462028.778 | -0.134 |  |  |
|  | $54.5 \leftarrow 53.5$ | 475202.141 | -0.040 | 470612.858 | 0.035 |  |  |
|  | $55.5 \leftarrow 54.5$ | 483866.644 | 0.052 | 479194.080 | 0.007 |  |  |
|  | $56.5 \leftarrow 55.5$ | 492528.241 | -0.028 | 487772.651 | 0.017 |  |  |
|  | $57.5 \leftarrow 56.5$ | 501187.170 | -0.017 | 496348.493 | 0.013 |  |  |
|  | $58.5 \leftarrow 57.5$ | 509843.376 | 0.054 | 504921.620 | 0.033 |  |  |
|  | $59.5 \leftarrow 58.5$ | 518496.647 | -0.003 | 513491.909 | -0.022 |  |  |
|  | $60.5 \leftarrow 59.5$ | 527147.131 | -0.019 | 522059.511 | 0.022 |  |  |
|  | $61.5 \leftarrow 60.5$ |  |  | 530624.216 | -0.025 |  |  |
| (020) $\Gamma_{9 / 2}$ | $42.5 \leftarrow 41.5$ | 371325.920 | -0.004 | 367789.027 | -0.050 |  |  |
|  | $43.5 \leftarrow 42.5$ | 380038.790 | 0.011 | 376419.105 | -0.019 |  |  |
|  | $44.5 \leftarrow 43.5$ | 388749.955 | 0.012 | 385047.501 | -0.008 |  |  |
|  | $45.5 \leftarrow 44.5$ | 397459.418 | 0.039 | 393674.248 | 0.053 |  |  |
|  | $46.5 \leftarrow 45.5$ | 406167.071 | 0.025 | 402299.179 | 0.036 |  |  |
|  | $50.5 \leftarrow 49.5$ | 440979.217 | -0.044 | 436780.858 | 0.065 |  |  |
|  | $51.5 \leftarrow 50.5$ | 449677.396 | -0.110 | 445396.443 | -0.036 |  |  |
|  | $52.5 \leftarrow 51.5$ | 458373.672 | -0.079 | 454010.168 | -0.030 |  |  |

EPAPS Table 1. Cont'd.

| $\left(v_{1}, v_{2}, v_{3}\right) K_{P}$ | $\mathrm{J}+1 \leqslant \mathrm{~J}$ | ${ }^{38} \mathrm{NiCN}$ |  | ${ }^{60} \mathrm{NiCN}$ |  | ${ }^{62} \mathrm{NiCN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $V_{\text {obs }}$ | $v_{\text {coss }}-v_{\text {calc }}$ | $v_{\text {dess }}$ | $v_{\text {dus }}-v_{\text {cadc }}$ | $\mathrm{V}_{\text {obs }}$ | $\nu_{\text {dbs }}-\nu_{\text {calc }}$ |
| (020) $\Gamma_{9,2}$ | $53.5 \leftarrow 52.5$ | 467067.989 | 0.034 | 462621.902 | -0.010 |  |  |
|  | $54.5 \leftarrow 53.5$ | 475760.189 | 0.108 | 471231.552 | -0.030 |  |  |
|  | $55.5 \leftarrow 54.5$ | 484450.123 | 0.034 | 479839.199 | 0.028 |  |  |
|  | $56.5 \leftarrow 55.5$ | 493137.917 | -0.024 |  |  |  |  |
| (030) $\Phi_{7 / 2}$ | $42.5 \leftarrow 41.5$ | 373187.244 | 0.054 | II |  |  |  |
|  | $43.5 \leftarrow 42.5$ | 381941.911 | -0.051 |  |  |  |  |
|  | $44.5 \leftarrow 43.5$ | 390694.905 | -0.009 |  |  |  |  |
|  | $45.5 \leftarrow 44.5$ | 399445.991 | -0.010 |  |  |  |  |
|  | $51.5 \leftarrow 50.5$ | 451910.773 | 0.011 |  |  |  |  |
|  | $53.5 \leftarrow 52.5$ | 469381.978 | 0.041 |  |  |  |  |
|  | $54.5 \leftarrow 53.5$ | 478114.078 | -0.013 |  |  |  |  |
|  | $55.5 \leftarrow 54.5$ | 486843.878 | -0.004 |  |  |  |  |
|  | $56.5 \leftarrow 55.5$ | 495571.238 | -0.016 |  |  |  |  |
|  | $57.5 \leftarrow 56.5$ | 504296.139 | -0.009 |  |  |  |  |
|  | $59.5 \leftarrow 58.5$ | 521738.255 | -0.007 |  |  |  |  |
|  | $60.5 \leftarrow 59.5$ | 530455.369 | 0.013 |  |  |  |  |
| (030) $\mathrm{H}_{112}$ | $42.5 \leftarrow 41.5$ | 373239.057 | -0.042 |  |  |  |  |
|  | $43.5 \leftarrow 42.5$ | 381995.804 | -0.035 |  |  |  |  |
|  | $44.5 \leftarrow 43.5$ | 390750.852 | 0.042 |  |  |  |  |
|  | $45.5 \leftarrow 44.5$ | 399503.953 | -0.019 |  |  |  |  |
|  | $46.5 \leftarrow 45.5$ | 408255.289 | 0.006 |  |  |  |  |
|  | $50.5 \leftarrow 49.5$ | 443241.239 | 0.028 |  |  |  |  |
|  | $51.5 \leftarrow 50.5$ | 451982.690 | 0.030 |  |  |  |  |
|  | $52.5 \leftarrow 51.5$ | 460721.934 | -0.081 |  |  |  |  |
|  | $53.5 \leftarrow 52.5$ | 469459.275 | 0.040 |  |  |  |  |
|  | $54.5 \leftarrow 53.5$ | 478194.327 | 0.048 |  |  |  |  |
|  | $55.5 \leftarrow 54.5$ | 486927.149 | 0.042 |  |  |  |  |
|  | $56.5 \leftarrow 55.5$ | 495657.641 | -0.037 |  |  |  |  |
|  | $57.5 \leftarrow 56.5$ | 504385.989 | 0.038 |  |  |  |  |
|  | $58.5 \leftarrow 57.5$ | 513111.882 | -0.003 |  |  |  |  |
|  | $59.5 \leftarrow 58.5$ | 521835.432 | -0.009 |  |  |  |  |
|  | $60.5 \leftarrow 59.5$ | 530556.525 | -0.052 |  |  |  |  |
| (100) $\Delta_{5 / 2}$ | $51.5 \leftarrow 50.5$ | 443527.127 | 0.049 | 439291.606 | 0.139 |  |  |
|  | $52.5 \leftarrow 51.5$ | 452088.316 | 0.055 | 447771.446 | 0.019 |  |  |
|  | $53.5 \leftarrow 52.5$ |  |  | 456248.675 | -0.149 |  |  |
|  | $54.5 \leftarrow 53.5$ | 469202.627 | -0.154 | 464723.538 | -0.101 |  |  |
|  | $55.5 \leftarrow 54.5$ | 477756.015 | -0.069 | 473195.794 | -0.062 |  |  |
|  | $56.5 \leftarrow 55.5$ | 486306.707 | -0.022 | 481665.450 | -0.011 |  |  |

EPAPS Table 1. Cont'd.

| $\left(v_{1}, v_{2}, v_{3}\right) K_{p}$ | $1+1 \leftarrow 1$ | ${ }^{58} \mathrm{NiCN}$ |  | ${ }^{20} \mathrm{NiCN}$ |  | ${ }^{52} \mathrm{NiCN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $V_{\text {dos }}$ | $\nu_{\text {cbse }}-\nu_{\text {calc }}$ | $\nu_{\text {doss }}$ | $v_{\text {orss }}-\nu_{\text {calc }}$ | $V_{\text {obs }}$ | $\mathrm{V}_{\text {bbs }}-V_{\text {calc }}$ |
| (100) $\Delta_{5 / 2}$ | $57.5 \leftarrow 56.5$ | 494854.744 | 0.040 | 490132.536 | 0.097 |  |  |
|  | $58.5 \leftarrow 57.5$ | 503400.100 | 0.102 | 498596.846 | 0.067 |  |  |
|  | $59.5 \leftarrow 58.5$ | 511942.686 | 0.085 | 507058.569 | 0.095 |  |  |
|  | $60.5 \leftarrow 59.5$ | 520482.503 | -0.006 | 515517.519 | 0.006 |  |  |
|  | $61.5 \leftarrow 60.5$ | 529019.635 | -0.080 | 523973.794 | -0.100 |  |  |

EPAPS Table 2. Measured Rotational Transitions of the $v_{2}=1:{ }^{2} \Pi_{3 / 2}$ Vibronic State of $\mathrm{NiCN}\left(\mathrm{X}^{2} \Delta_{\mathrm{i}}\right)^{\text {a }}$

| $\mathrm{J}+\mathrm{I} \leftarrow \mathrm{J}$ | Parity | ${ }^{58} \mathrm{NiCN}$ |  | ${ }^{66} \mathrm{NiCN}$ |  | ${ }^{62} \mathrm{NiCN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $v_{\text {ots }}$ | $V_{\text {ols }}-\nu_{\text {cealc }}$ | $V_{\text {chss }}$ | $V_{\text {obs }}-V_{\text {calc }}$ | $\nu_{\text {cts }}$ | $\nu_{\text {dxs }}-v_{\text {calc }}$ |
| $43.5 \leftarrow 42.5$ | f | 378044.708 | -0.024 | 374447.190 | -0.023 |  |  |
|  | e | . 378045.891 | -0.033 | 374448.289 | -0.083 |  |  |
| $44.5 \leftarrow 43.5$ | f | 386708.415 | -0.003 | 383028.666 | -0.057 |  |  |
|  | e | 386709.684 | 0.018 | 383029.937 | 0.002 |  |  |
| $45.5 \leftarrow 44.5$ | f | 395370.311 | 0.006 | 391608.550 | 0.083 |  |  |
|  | e | 395371.630 | 0.021 | 391609.776 | 0.042 |  |  |
| $46.5 \leftarrow 45.5$ | f | 404030.365 | 0.008 | 400186.457 | 0.047 | 396580.924 | 0.097 |
|  | e | 404031.758 | 0.039 | 400187.770 | 0.037 | 396582.164 | 0.022 |
| $47.5 \leftarrow 46.5$ | f |  |  | - |  | 405079.892 | -0.056 |
|  | e |  |  | 1 |  | 405081.270 | -0.050 |
| $50.5 \leftarrow 49.5$ | f | 438651.515 | 0.006 |  |  |  |  |
|  | e | 438653.125 | 0.009 |  |  |  |  |
| $51.5 \leftarrow 50.5$ | f | 447301.846 | -0.014 | 443047.863 | -0.036 |  |  |
|  | e | 447303.547 | 0.016 | 443049.580 | 0.058 |  |  |
| $52.5 \leftarrow 51.5$ | f | 455950.130 | -0.037 | 451614.296 | -0.017 | 447547.302 | -0.005 |
|  | e | 455951.914 | 0.010 | 451616.022 | 0.022 | 447548.973 | -0.010 |
| $53.5 \leftarrow 52.5$ | f | 464596.389 | -0.009 | 460178.708 | 0.020 | 456034.928 | 0.031 |
|  | e | 464598.178 | -0.023 | 460180.376 | -0.064 | 456036.598 | -0.039 |
| $54.5 \leftarrow 53.5$ | f | 473240.535 | 0.017 | 468740.914 | -0.076 | 464520.443 | -0.007 |
|  | e | 473242.347 | -0.043 | 468742.833 | 0.024 | 464522.240 | -0.016 |
| $55.5 \leftarrow 54.5$ | $f$ | 481882.477 | -0.019 | 477301.200 | 0.011 | 473003.885 | -0.049 |
|  | e | 481884.405 | -0.032 | 477303.044 | -0.031 | 473005.791 | -0.016 |
| $56.5 \leftarrow 55.5$ | f | 490522.296 | -0.003 | 485859.263 | 0.012 | 481485.284 | -0.032 |
|  | e | 490524.283 | -0.027 | 485861.184 | -0.021 | 481487.271 | 0.014 |
| $57.5 \leftarrow 56.5$ | f | 499159.882 | -0.013 | 494415.146 | 0.001 | 489964.587 | 0.020 |
|  | e | 499162.150 | 0.172 | 494417.137 | -0.032 | 489966.639 | 0.062 |
| $58.5 \leftarrow 57.5$ | f | 507795.251 | -0.001 | 502968.790 | -0.050 | 498441.645 | -0.009 |
|  | e | 507797.386 | -0.022 | 502971.053 | 0.118 | 498443.724 | -0.011 |
| $59.5 \leftarrow 58.5$ | f | 516428.391 | 0.052 | 511520.334 | 0.030 | 506916.575 | 0.029 |
|  | e | 516430.554 | -0.015 | 511522.460 | -0.011 | 506918.794 | 0.095 |
| $60.5 \leftarrow 59.5$ | f | 525059.140 | 0.015 | 520069.544 | 0,037 | 515389.235 | 0.020 |
|  | e | 525061.361 | -0.070 | 520071.720 | -0.027 | 515391.436 | -0.004 |
| $61.5 \leftarrow 60.5$ | f |  |  | 528616.429 | 0.011 | 523859.585 | -0.043 |
|  | e |  |  | 528618.704 | -0.030 | 523861.928 | $<0.000$ |
| $62.5 \leftarrow 61.5$ | f |  |  |  |  | 532327.774 | 0.017 |
|  | e |  |  |  |  | 532330.073 | -0.060 |

a) $\ln \mathrm{MHz}$

EPAPS Table 3. Measured Rotational Transitions of the $\mathrm{V}_{2}=2:{ }^{2} \Sigma_{12}$ Vibronic State of $\left.\operatorname{NiCN}\left(\mathrm{X}^{2} \Delta_{\mathrm{i}}\right)^{2}\right)$

| $\mathrm{N}+1 \leftarrow \mathrm{~N}$ | $\mathrm{j}+1 \leftarrow \mathrm{~J}$ | ${ }^{38} \mathrm{NiCN}$ |  | ${ }^{65} \mathrm{NiCN}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $V_{\text {obs }}$ | $V_{\text {cbs }}-V_{\text {casle }}$ | Vobs | $v_{\text {cbs }}-v_{\text {cals }}$ |
| $42 \leftarrow 41$ | $42.5 \leftarrow 41.5$ | 371290.957 | -0.069 | 367754.767 | -0.032 |
| $43 \leftarrow 42$ | $42.5 \leftarrow 41.5$ | 371329.692 | 0.027 | 367792.969 | 0.009 |
| $43 \leftarrow 42$ | $43.5 \leftarrow 42.5$ | 380003.484 | -0.038 | 376384.485 | -0.023 |
| $44 \leftarrow 43$ | $43.5 \leftarrow 42.5$ | 380042.323 | 0.037 | 376422.730 | -0.052 |
| $44 \leftarrow 43$ | $44.5 \leftarrow 43.5$ | 388714.360 | 0.029 | 385012.481 | -0.078 |
| $45 \leftarrow 44$ | $44.5 \leftarrow 43.5$ | 388753.240 | 0.016 | 385051.009 | 0.060 |
| $45 \leftarrow 44$ | $45.5 \leftarrow 44.5$ | 397423.441 | 0.026 | 393638.942 | 0.027 |
| $46 \leftarrow 45$ | $45.5 \leftarrow 44.5$ | 397462.455 | 0.015 | 393677.401 | -0.022 |
| $46 \leftarrow 45$ | $46.5 \leftarrow 45.5$ | 406130.811 | 0.076 | 402263.576 | 0.039 |
| $47 \leftarrow 46$ | $46.5 \leftarrow 45.5$ | 406169.813 | -0.081 | 402302.163 | -0.003 |
| $50 \leftarrow 49$ | $50.5 \leftarrow 49.5$ | 440941.624 | 0.026 | 436743.972 | 0.043 |
| $51 \leftarrow 50$ | $50.5 \leftarrow 49.5$ | 440981.235 | -0.088 | 436783.011 | -0.057 |
| $51 \leftarrow 50$ | $51.5 \leftarrow 50.5$ | 449639.567 | 0.051 | 445359.374 | 0.062 |
| $52 \leftarrow 51$ | $51.5 \leftarrow 50.5$ | 449679.368 | -0.022 | 445398.614 | 0.028 |
| $52 \leftarrow 51$ | $52.5 \leftarrow 51.5$ | 458335.366 | -0.071 | 453972.830 | 0.097 |
| $53 \leftarrow 52$ | $52.5 \leftarrow 51.5$ | 458375.452 | -0.011 | 454012.188 | 0.044 |
| $53 \leftarrow 52$ | $53.5<52.5$ | 467029.293 | -0.030 | 462584.184 | 0.030 |
| $54 \leftarrow 53$ | $53.5 \leftarrow 52.5$ | 467069.610 | 0.107 | 462623.714 | 0.010 |
| $54 \leftarrow 53$ | $54.5 \leftarrow 53.5$ |  |  | 471193.473 | -0.065 |
| $55 \leftarrow 54$ | $54.5 \leftarrow 53.5$ |  |  | 471233.234 | 0.005 |
| $55 \leftarrow 54$ | $55.5 \leftarrow 54.5$ |  |  | 479800.741 | -0.103 |
| $56 \leftarrow 55$ | $55.5 \leftarrow 54.5$ |  |  | 479840.656 | -0.025 |

a) $\ln \mathrm{MHz}$.

## APPENDIX H

## ROTATIONAL REST FREQUENCIES FOR FeN ( $\mathrm{X}^{2} \triangle_{i}$ ) AND REVISED SPECTROSCOPIC CONSTANTS FOR FeC ( $X^{3} \Delta_{i}$ )

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ROTATIONAL REST FREQUENCIES FOR FEN ( $X^{2} A$ ) AND REVISED SPECTROSCOPIC CONSTANTS FOR FEC ( $A^{3} A$ ) P. M. Sheridan and E. M. Zurys

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## ABSTRACT

The pure rotational spectum of FeN in its $\mathcal{H}^{2} A$, ground state has been recorded using millineuer-wave direct absorption techniques in the range $198-525 \mathrm{GHz}$. New measuremens have also been carried out for $\mathrm{FeC}\left(X^{3} \Delta_{1}\right)$, in particular of the $\Omega=1$ fine-structure component and the ${ }^{3} \mathrm{FeC}$ isotopomer. These molecules were created by the reaction of iron vapor with either $\mathrm{CH}_{4}(\mathrm{FeC})$ or $\mathrm{N}_{2}(\mathrm{FeN})$ in a DC discharge. Eight rotational transivions were recorded for FeN in its lowest-lying spin component, $\mathfrak{D}=5 / 2$, and mulifple transitions were measured for FeC in all three of its spinoorbit ladders, as well as for ${ }^{56} \mathrm{FeC}(\Omega=3)$. These dara have been analyzed, and precise spectroscopic constants for both radicals have been determined. The fine structure in FeC was found to exhibit an irregular pattem, indicating that higher order spin-orbit perturbations are occurring in this molecule. Although only one spin component was observed for FeN, the bond length established from the $\mathrm{D}=5 / 2$ data is consistent with a ${ }^{2} \Delta$ ground state, as indicated by theory. Fe-bearing species are relevant io many astrophysical topics, including astrochemisty, dust grains composition, nucleosynthesis, and mass loss from asymplotic gians branch stars.
Subject headings: astrochemisury - 1SM: molecules - line: identification - methods: laboratory molecular dats - stars: AGB and post-AGB

1. ANTRODUCTION

Iron is known to play an important role in a variety of astrophysical environments. For instance, this element is central to nucleosynthesis. Not only is ${ }^{50}$ Fe the most stable naturally occurring nucleus, and hence the end product of silicon buming, but it is thought to be preferentially made by Type Ia supemovae (e.g., Hughes et al. 2003). Therefore, the interstelliar Fe abundance is thought to be a direct indicator of the Type Ia occurrence rate. Iron is also important for interstellar grains (e.g., Zinner 1998). Calcium-aluminum-rich inclusions in meteories contain iron, for example.
Because iron is central to many astrophysical themes, it is useful to study this element in molecular forn. Various aluminurn, magnesium, and sodium-bearing molecules have in fact already been detected in circumstellar envelopes of asymptotic giant branch (AGB) and post-AGB stars (e-g., Highberger et al. 2001). These species have provided a means of evaluating isotope ratios such as ${ }^{24} \mathrm{Mg}:{ }^{25} \mathrm{Mg}:{ }^{26} \mathrm{Mg}$ (Guelin et al. 1995), yielding observational constraints of $A G B$ nucleosynthesis. Measurements of isotope ratios such as ${ }^{50} \mathrm{Fe}{ }^{39} \mathrm{Fe}$ would clearly be of interest.

Two iron-containing molecules that might be of use for such investigations are FeC and FeN . Originally observed in the laboratory by laser-induced fluorescence (LiF) methods (Balfour et al. 1995), the pure rocational spectrum of FeC in its $X$ ${ }^{3} A$, ground electronic state was subsequentiy recorded by Allen, Pesch, \& Ziurys (1996). However, both these studies measured only two of the three possible fine-structure components in this radical ( $\mathfrak{A}=3$ and $\mathbb{D}=2$ ). More recent studies using nearinfrared laser diode spectroscopy by Leung et al. (2001) and Fujitake et al. (2001) have resulted in the idenification of a nearby ' $\Delta$ state, as well as the $\mathbb{m}=1$ component in the ${ }^{3} \Delta$

[^9]ground state. Both sets of authors found unequal energy spacings between the three spin ladders in the ground state, suggesting that the $\Omega=2$ level was perturbed by the excited ${ }^{\text {t }} \Delta$ state. This perturbation made it more difficult to locate the $\square=1$ component in the previous investigations.
For FeN, laboratory data thus far have been confined to one suady: LIF spectroscopy by Aiuchi \& Shibuya (2000). Various electronic transitions were recorded in this work, which all originated from an electronic ground stare that had the quantum number $\mathbb{I}=5 / 2$. These authors therefore concluded that the ground state temm was either ${ }^{2} \Delta$ or ${ }^{4}$ II but could not distinguish between chem. Previous ab initio calculations by Fielder \& Iwava (1997) had suggested four possibilities for the ground


In this Lerter, we present measurements of the pure rotational spectra of FeN in its lowest energy spin component, $D=$ $5 / 2$. Alwhough the $\AA=3 / 2 \mathrm{spin}$ ladder was not observed, this work is consistent with the ground state of FeN being ${ }^{2} \Delta_{\text {. }}$ Spectra of FeC in is $\Omega=1$ spin level have also been recorded, which has emabled a complete set of spectroscopic parameters for this radical in its $X^{3} \Delta_{\text {, }}$ state to be determined. In addition, new measurements of the ${ }^{34} \mathrm{Fe}$ isotopomer in the I $=3$ ladder have been oblained.

## 2. EXPERIMENTAL

The measurements were conducted using the high-temperaure millimeter/submillimeter direct absorption spectrometer of the Ziurys group. This instrument is similar to that described in Ziurys et al. (1994), except the optics scheme employs offset ellipsoidal mirrors as focusing elements, along with a pathlength modulator for improved baseline stability. Also, the reaction chamber has a double-walled construction for maximum cooling.

Both FeC and FeN were synthesized by the reactim of iron

TABLE
Measumen Rotatromal Thansityon Frequencien (in Molz) $0 \operatorname{FeN}\left(X^{2} \Delta_{1}\right)$ and Fec $\left(X^{\prime} \Delta_{1}\right)$

| Isacorge | I | $J+1$ | 8 | $y_{\text {zem }}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| FeN | 4.5 | $\$ .5$ | 2.5 | 198763.244 | 0.647 |
|  | \$3 | 6.5 | 2.5 | 234890.645 | -0.039 |
|  | 85 | 9.3 | 25 | 343235.822 | -0.019 |
|  | 9.5 | 10.5 | 2.5 | 379335.603 | 0.035 |
|  | 10.5 | 18.5 | 25 | 415426.173 | -0.014 |
|  | 11.5 | 12.5 | 25 | 451506.840 | 0.018 |
|  | 12.5 | 135 | 2.5 | 487576.598 | -0.032 |
|  | 13.5 | 145 | 25 | 523634.739 | 0.020 |
| afec $\ldots .$. | 5 | 6 | 3 | 240862.951 | -0.004 |
|  | 5 | 6 | 2 | 242020.332 | 0.004 |
|  | 5 | 6 | 1 | 242480.360 | 0.013 |
|  | 6 | 7 | 3 | 280989.165 | -0.002 |
|  | 6 | 7 | 2 | 282338.846 | 0.006 |
|  | 6 | 7 | 1 | 282875.360 | -0.002 |
|  | 7 | 8 | 3 | 321107.258 | 0.009 |
|  | 7 | 8 | 2 | 322648.906 | 0.018 |
|  | 7 | 8 | 1 | 323261.883 | -0.012 |
|  | 8 | 9 | 3 | 361216.048 | 0.009 |
|  | 8 | 9 | 2 | 362949.825 | -0.027 |
|  | 8 | 9 | 1 | 363638.720 | $-0.015$ |
|  | 9 | 10 | 3 | 401314.372 | -0.004 |
|  | 9 | 10 | 2 | \$03239.152 | $\leqslant 0.000$ |
|  | 9 | 10 | 1 | 404004.677 | 0.006 |
|  | 10 | 11 | 3 | 441401.086 | -0.012 |
|  | 10 | 11 | 2 | 443516.843 | -0.003 |
|  | 10 | 11 | 1 | 444358.526 | 0.034 |
|  | 11 | 12 | 3 | 481475.045 | 0.002 |
|  | 11 | 12 | 2 | 483781.334 | -0.001 |
|  | 11 | 12 | 1 | 484698.957 | -0.027 |
|  | 12 | 13 | 3 | 521335.053 | D.004 |
|  | 12 | 13 | 2 | 524031.424 | 0.006 |
|  | 12 | 13 | 1 | 525024.944 | 0.005 |
| ${ }^{20} \mathrm{FeC} . . . . . .$. | 6 | 7 | 3 | 282810.884 | -0.057 |
|  | 8 | 9 | 3 | 363557.572 | 0.069 |
|  | 9 | 10 | 3 | 403915.631 | 0.060 |
|  | 12 | 13 | 3 | 524914.234 | -0.021 | ea al. 1996.

vapor, created in a high-ternperature Broida-type oven, with an appropriate precursor mixture in the presence of a DC discharge. To produce FeC. approximately $10-15$ miorr of CH was mixed with 20 morr of argon and then adided through the boiom of the oven to entrain the metal vapor. The complate mixture was then discharged, using a current of 0.7-1.0 A at 200 V. A similar production method was employed in our previous study of Fec by Allea ef al. (1996), cxcept belium was substituted for argon. To synthesize FeN, about $15-20$ morr of pure $\mathrm{N}_{2}$ was used for the reaction under similigr discharge conditions.

Searches for the $\mathbb{Q}=1$ ledder of FeC and the $2=5 / 2$ coms. ponent of FeN were based on predictions using rotational constants from Leung el al. (2001), Fujitake al. (2001), giad Aivachi \& Shibuya (2000). In the course of recording the $D=1$ data, it was realized that the frequencies were identical to lines previously atributed to the $2=3$ ladder of ${ }^{59} \mathrm{FeC}$ by Allen et al. (1996). They had been misassigned because of the irregrelar spliting of the 1 components. In fact, Fujitake ea al. had obtained 5 Fec das in the ground stake and mentioned hat the rotational constant was extremely close to that of the $Q=1$ component of ${ }^{3} \mathrm{FeC}$. A renewed search for the ${ }^{50} \mathrm{Fec}$ lines $(\Omega=3)$ was consequently conducted, and in the process additional transitions of ${ }^{56} \mathrm{FeC}$ in the $A=3$ and 2 ladders were recorded. Final measurements were established from averages of one to as many 2545 scan pairs, with each pair consisting


Frc. 1.-Stick spectrum of the $y=9 \rightarrow 10$ rotational aransition of FeC in its $X^{3} \mathrm{~A}$, tround seate mear 402 GHz (app panel) and a represensabive laboratcory spectrum of severtil of these feanures near 409 GHz (bortom panel). The stick spretrexa shows the atree spin components of FeC that compsise this transizion, tabeled by quarrum snamber a These fesomes do noc show a regular criplea patuen; the $\mathbb{D}=2$ lime is eppparently percurbed and thenefore shifued so thigher fregremery. The posinion of the she isompormer in the $1=3$ ladder is eltoo showni. The messured spectram (bozsom panel) displays the $\Omega=1$ spin come

 was erated fromp two 100 MHz scans, exch 1 zainute in duration.
of one scan in increasing and another in decreasing frequency over a 5 MH iz range. The averages were then fited io Gaussian profiles in order to determine the center frequeacy. Over the measurement range of $190-530 \mathrm{GHz}$, the line widths varied from 600 to 1300 kHz.

## 3. RESULTS AND ANALYSIS

Eight rotational transitions were recorded for FeC in its $0=1$ spin-orbit component and an identical number for $F e \mathrm{~N}$ in its $0=5 / 2$ level. These measurements are presented in Table i, as well as the transition frequencies for the $\rrbracket=3$ and 2 fine-structure comporents of FeC , about half of which are newly measured. (The remainder is from Allem et al. 1996; the later values are listed because they were included in the data fil) It should be noted that the three $\cap$ components are not evenly separated in frequency. Also listed in the table are four transitions recorded for the $\AA=3$ ladder of the ${ }^{s} \mathrm{Fe}$ isotopomer of iron carbide.

Figure 1 displays a stick Gure of the $J=9 \rightarrow 10$ transition of FeC near 402 GHz (top pranen), and the actual measured spectrum of the ${ }^{56} \mathrm{FeC}(\Omega=1)$ and the ${ }^{54} \mathrm{FeC}(\Omega=3)$ lines (bottom pone). In the top panel, the actual position of the B $=2$ component is shown, as well as its "unperuarbed" lo-


Finc. 2-Specaram of the $a=5 / 2$ component of the $J=9.5 \rightarrow 10.5$ sorscional aransition of FeN ( $A^{2} A$, , observed in the laboralcry mear 379 GH 2 The FeN signaks are much weaker than those of FeC (cf. Fig. 1), indicating a more difficuin mofecular symbesis. These doan comprise a aingle, 100 MHz scan oberined in 1 minuse.
cation, which is midway between the other two 1 components. This shift is in part dere to isoconfigurational second-order spinorbit coupling, caused by the a $a^{\prime} A_{2}$ excited state (Leung et al. 2001; Fujitate et al. 2001). This state, which lies more than $3000 \mathrm{~cm}^{-1}$ higher in energy, perurbs the $\Omega=2$ level in the ground state and effectively lowers its energy by $-30 \mathrm{~cm}^{-1}$. This energy shift manifests itself in the pure rotational spectum as asymmetric splituings between the 10 componens. As illustrated in the lower panel of Figure 1, the ${ }^{34} \mathrm{FeC}$ feature (on the leff) is much less intense than the ${ }^{30} \mathrm{FeC}, \mathbf{a}=1$ line (on the right), following the natural iron isotope ratio of ${ }^{50} \mathrm{Fe}$ : ${ }^{34} \mathrm{Fe}=91.7: 5.8$. It is also interesting to note that the $\mathbf{\Omega}=1$ component in FeC does not exhibit lambda-doubling.

The observed signals for FeN in the main iron isotope are relatively weak, as shown in Figure 2. Here the observed spectrum of the $J=9.5 \rightarrow 10.5$ rotational transition of this radical in its $\rrbracket=5 / 2$ ladder is presented. Despite the fact that this component has the lowest energy of the fine-structure manifold for FeN , it is not nearly as intense as the line in the $\mathrm{D}=$
ladder of FeC . This difference reflects the relative difficulty in synthesizing the nitride relative to the carbide.
The saleC data were analyzed using the following case (a) Hamiltonian:

$$
\begin{equation*}
\hat{H}_{\mathrm{str}}=\hat{H}_{\mathrm{soc}}+\hat{H}_{\mathrm{so}}+\hat{H}_{\mathrm{ss}} . \tag{1}
\end{equation*}
$$

Thus, rotational motion and spin-orbia and spin-spin interactions were included in the data fit. Spectroscopic parameters determined from this analysis are presented in Table 2, along with previous constants from Allea et al. (1996) and Fujitake et al. (2001). As the table shows, the new parameters are all well determined. The large errors on $A$, the spin-arbit constant, and $\lambda$, the spin-spin constant, are expected as direct measurement of the fine-structure energies is not achievable by pure rotational spectroscopy. The differences betweem the cument values and those of Allen et al. result from the addition of the new $\Omega=1$ data. The spin-orbil constant derived from this analysis ( $A=-4,969,000 \mathrm{MHz}=-165.7 \mathrm{~cm}^{-8}$ ) is very close to the equilibrium value of $A_{c}=-178.7 \mathrm{~cm}^{-1}$ from Fu jitake et al. (2001). Some differences ane also apparemt between the millimeter-wave constants and those of Fujitake ef al. because these authors fixed the spin-spin parameter to zero. In contrast, the millimeter-wave FeC data could not be fited withons $\lambda$.
Spectroscopic constants determined for ${ }^{50} \mathrm{FeC}(\Omega=3)$ and FeN ( $0=5 / 2$ ) are presented in Table 2 as well. Because in both cases one single fine-structure ladder was observed, only $B$ and $D$ were established. These constants agree well with those derived from optical/IR data.

## 4. DISCUSSION

This study has resulted in the first complete set of rotational constants for FeC with the accuracy required for astronomical searches; a revised bond length of $r_{0}=1.5931 \AA$ has been determined as well. It has also provided revised frequencies and constants for ${ }^{50} \mathrm{FeC}$ in its lowest fine-structure level. Rest frequencies have additionally been measured for FeN.
As discussed by Balfour et al. (1993), equal splitings of the fine-structure cormponents in a ${ }^{3} \Delta$ state occur in the absence of higher order spin-orbit coupling and direct spin-spin interactions. The parameter $\lambda$ contains contributions from both effects.

TABLE 2
Spectroscopic Pamametick for Fen and Fec

| Isoupe | Pamametar | Vare (MHz) | Pas Sandies (MHz) |
| :---: | :---: | :---: | :---: |
| FeN ( $\left.H^{7} \triangle\right)$ : $2=3 / 2 \ldots \ldots$ | $\stackrel{8}{8}$ | 18,071.5683 (76) | $18,071.3$ [1.5) |
|  | $D$ | 0.036144 (24) | 0.0363 (37) |
|  | mias of fit | 0.030 |  |
| ${ }^{s} \mathrm{Fec}\left(\mathrm{H}^{3} \mathrm{~A}_{1}\right) \ldots \ldots \ldots \ldots .$. | $B$ | $20,152.7619(14)$ | $20.173 .4036(19)^{\circ}$ |
|  | D | 0.0496334 (56) | $0.0500739(80)^{\circ}$ |
|  | $A$ | $-4,999000(39,000)$ | $-5,358,500$ (3300) |
|  | $A_{0}$ | 9.35 (30) | $4.66852(61)^{4}, 3.64221(59)^{6}$ |
|  | $\lambda$ | 1,285,000 (43,000) |  |
|  | $\lambda_{0}$ | 18.2 (1.0) | $-3.0642(86)^{*}$ |
|  | mane of fin | 0.015 |  |
| $\operatorname{sFeC}\left(X^{2} A_{i}\right): 8=3 \ldots \ldots$ | $B$ | 20,205.588 (11) | 20,203.5 (2.4) |
|  | D | 0.049049 (42) | 0.04902 |
|  |  | 0.043 |  |

Notit-Errors ane 30 and apply to the last quoted decimal places.

${ }^{2}$ From Allen ef al 1996; measurements of $0=3$ and 2 spin-artir conmponems only


Because the pure spin-spin interaction is roughly proportional so $1 / Z$, where $Z$ is the atomic number, the higher order spinorbit perturbations will likely dominate in a beavier molecule such as FeC. The main contributor so this higher order intepo action in FeC is the a ' $\triangle$ state, which perurbs the $1=2$ level only. If this interaction is indeed the primary cause of umequal fine-structure splittings in FeC, then $\lambda$ should reflect this perturbation. In this case, the ${ }^{1} \Delta-^{3} \Delta$ energy difference cans be calculated using the following expression, based on first-order perturbacion theory (Balfour at al. 1993):

$$
\begin{equation*}
\Delta E=4 \lambda+\frac{A^{2} A^{2}-4 \lambda^{2}}{2 \lambda} \tag{2}
\end{equation*}
$$

Using the values for $A$ and $\lambda$ from Table 2, the ' $\Delta-^{3} \Delta$ energy separation was foumd to be $A E \approx 1368 \mathrm{~cm}^{-1}$. The actual energy difference is $3465 \mathrm{~cm}^{-1}$ (Leung ef al. 2001). This discrepancy suggests that additional excited states are perturbing the ground state; the ${ }^{3}$ state, which is calculated to lie $15,300 \mathrm{~cm}^{-1}$ higher in energy (Shim \& Gingerich 1999), is a likely candidate. The ${ }^{\prime}$ III ' ' $\Phi$, and ${ }^{3}$ ' states are also other possibilities.
The energy shif of the perturbed $a=2$ level can be estimated from the rotstional constants and $A_{b}$, the centrifugal distortion conrection to the spin-orbit constamt, using the following expressions (Fujitake et al. 2001):

$$
\begin{align*}
& \Lambda A+\Delta E=\frac{2\left(B+A_{D}\right)^{2}}{B(M=3)-2 A_{D}-B} \\
& \Lambda A-\Delta E=\frac{-2\left(B-A_{D}\right)^{2}}{B(M=1)+2 A_{D}-B} \tag{3}
\end{align*}
$$

Using the millimeter-wave constants in Table 2 and $B$-values for the individual $\Omega$ ladders, derived from the data in Table 1 , the energy shifl is estimated to be $\Delta E=36 \mathrm{cms}^{-1}$, for $\Lambda A=$
$-318.6 \mathrm{~cm}^{-1}$, or $A=-159.3 \mathrm{~cm}^{-8}$. The actual value of $\Delta E$ is $30 \mathrm{~cm}^{-1}$. The calculated and measured numbers are certainily in reasomable agreement, lending additional credibility to the maxlysis.
Other A states exhibit lambda-doubling in several of their spin-orbit components. For example, this interaction is apparent in the $\Omega=-1 / 2,1 / 2$, and $3 / 2$ ladders in the $X^{*} A$ states of both FeF and FeCl (Allen \& Zurys 1997; Allea, Li, \& Ziurys 1997. NiCN and NiH exhibit lambdr-doubling in the $\mathbb{D}=$ $3 / 2$ ladder of their $X^{3} A_{1}$ states (Sheridan 名 Ziurys 2003; Nelis et al. 1991). In contrast, lambda-doubling is not present in FeC even in the $\mathbb{Q}=1$ ladder, where the matrix elements for this interaction enver in as a ciagonal ecm (Browa, Cheung, \& Merer 1987). Lambda-doubling is caused by perturbations by nearby excited electronic states, in particular ${ }^{3}$ II, ${ }^{1} 1 I, 15$, and ${ }^{5} \mathrm{te}$ terms for ${ }^{2} \Delta$ grourd states. As suggested by ab initio calculations (Shim \& Gingerich 1999; Tzeli \& Mavridis 2002), such states exist in the FoC manifold, bust with the exception of a ${ }^{3} \mathrm{E}^{-}$state, lie quite high in energy (i.e. $>15,000 \mathrm{~cm}^{-1}$ ). Because the magnitudie of the lambda-doubling interaction is izversely proportional to the energy differences between the ground and perturbing excited states, the effect of these highlying levels is mitigated. Based on the measured line widtus, an upper limit of 10 kHz can be estimated for the main A . doubling constans, $\tilde{o}_{4}$, in FeC .
T. Hirano (2003, in preparation) has done additional ab initio calculations for FeN , which indicate $a^{2} \mathrm{~A}_{i}$ ground state with a bond length of $r_{c}=1.5784 \dot{A}$; for the II state, $r_{0}$ was calculated to be $1.5944 \AA$. The bond length measured here, based on the $\emptyset=5 / 2$ component, is $r_{0}=1.5802 \mathrm{~A}$. If other spin-orbit ladders were included, the bond length would be even shorter, consistent with the ${ }^{2} \Delta$ term and not with a ${ }^{4} \Pi$ state.

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## APPENDIXI

THE PURE ROTATIONAL SPECTRUM OF TIF ( $\mathrm{X}^{4} \Phi_{\mathrm{I}}$ ): 3d TRANSITION METAL FLUORIDES REVISITED
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The Pure Rotational Spectrum of TiF $\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$ : 3d Transition Metal

## Fluorides Revisited

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#### Abstract

The pure rotational spectrum of TiF in its $X^{4} \Phi_{r}(v=0)$ ground state has been measured using millimeter/sub-millimeter wave direct absorption techniques in the range $140-530 \mathrm{GHz}$. In ten out of the twelve rotational transitions recorded, all four spin-orbit components were observed, confirming the ${ }^{4} \Phi_{r}$ ground state assignment. Additional small splittings were resolved in several of the spin components in lower J transitions, which appear to arise from magnetic hyperfine interactions of the ${ }^{19} \mathrm{~F}$ nucleus. In contrast, no evidence for $\Lambda$-doubling was seen in the data. The rotational transitions of TiF were analyzed using a case (a) Hamiltonian, resulting in the determination of rotational and fine structure constants, as well as hyperfine parameters for the fluorine nucleus. The data were readily fit in a case (a) basis, indicating strong first order spin-orbit coupling and minimal second-order effects, as also evidenced by the small value of $\lambda$, the spin-spin parameter. Moreover, only one higher order term, 7 , the spin-orbit/spin-spin interaction term, was needed in the analysis, again suggesting limited perturbations in the ground state. The relative values of the $a, b$, and $c$ hyperfine constants indicate that the three unpaired electrons in this radical lie in orbitals primarily located on the titanium atom and support the molecular orbital picture of TiF with a $\sigma^{1} \delta^{1} \pi^{1}$ single electron configuration. The bond length of TiF ( $1.8342 \AA$ ) is significantly longer than that of TiO , suggesting that there are differences in the bonding between 3 d transition metal fluorides and oxides.


## 1. Introduction

Titanium is encountered in a wide variety of research areas. For example, because of its low density and exceptional corrosion resistance, the metal and its alloys are used in the construction of aircraft and marine vehicle equipment [1]. Metal oxides containing titanium have shown high dielectric and ferroelectric properties and thus appear to be useful in the design of microelectronic devices [2,3]. Titanium compounds are also employed as Ziegler-Natta type catalysts; cyclopentadienyl titanium species, for example, are used to polymerize olefins such as styrene and ethylene [4], while bis(phenoxyimine)-titanium based molecules are currently being investigated for their unique regioselectivity in polymerization insertion reactions [5]. From an astronomical aspect, gas-phase titanium bearing species such as TiO and TiH have been identified in the spectra of cool M-type stars [6,7], while titanium carbide crystals have been found in meteorites [8] and perhaps even in circumstellar gas [9].

Small titanium containing molecules are additionally of interest for gas phase spectroscopy. From their spectra, electronic and geometric properties of these species can be elucidated, leading to a better understanding of the macroscopic characteristics of larger Ti bearing compounds. Titanium has a $4 \mathrm{~s}^{2} 3 \mathrm{~d}^{2}$ valence electron configuration, however, such that Ti-bearing molecules usually have an extensive manifold of closely spaced electronic states which can perturb each other. Furthermore, high values of electron orbital and spin angular momenta often occur in such species. Despite these complexities, several titanium radicals have been studied to date via near-infrared and optical spectroscopy. For example, the $b^{l} \Pi$ $X^{3} \Delta$ transition of TiS, the ${ }^{4} \Gamma-X^{4} \Phi$ band of $T i H$, and the ${ }^{3} \Delta-X^{3} \Phi$ system of TiF ${ }^{+}$have been investigated $[10-12] ; \mathrm{TiF}\left(\mathrm{G}^{4} \Phi-\mathrm{X}^{4} \Phi\right)$ and $\mathrm{TiCH}\left({ }^{2} \Pi-\mathrm{X}^{2} \Sigma\right)$ have been studied as well [13, 14]. Millimeter-wave and PPMODR work have also been conducted, but thus far have been limited
to $\mathrm{TiO}\left(\mathrm{X}^{3} \Delta\right), \mathrm{TiN}\left(\mathrm{X}^{2} \Sigma\right)$, and $\operatorname{TiCl}\left(\mathrm{X}^{4} \Phi\right)[15,16]$. Hyperfine structure was observed in TiN, giving some insight into the bonding in titanium compounds.

One titanium radical of interest is TiF, partly because high resolution data on the 3d transition metal fluorides, in general, are limited. While electronic spectra of these species have been recorded [17-19], they are certainly not as well characterized as their oxide counterparts [20]. For example, pure rotational spectra exist only for $\mathrm{ScF}, \mathrm{CrF}, \mathrm{FeF}, \mathrm{NiF}$, and CuF [21-25]; in fact, only in the past year has the first high-resolution optical study of VF been conducted [17]. While these molecules are expected to exhibit highly ionic bonds, some, such as FeF [23], show signs of covalent character.

TiF has been the subject of relatively few spectroscopic investigations. It was first observed in absorption using flash heating techniques by Diebner and Kay in 1969, who assigned the ground state as ${ }^{4} \Sigma^{\prime}[26]$. Additional studies conducted by Chantalic, Deschamps, and Pannetier [27] again indicated a ${ }^{4} \Sigma$ ground state. Shenyavskaya and Dubov in 1985 conducted further optical work, resulting in the reassignment of the electronic ground term as ${ }^{2} \Delta$ [28]. Very recently, Ram et al. have observed the spectrum of TiF in emission by Fourier transform techniques and by laser excitation spectroscopy, performing the first rotational analysis [13]. In their work, the ground state of TiF was once again reassigned, this time as ${ }^{4} \Phi$. Their assignment was partly based on theoretical work by Harrison [29], and in analogy to $\mathrm{TiH}\left(\mathrm{X}^{4} \Phi\right)$ [11]. Subsequent calculations by Boldyrev and Simons [30] for TiF again suggested a ${ }^{4} \Phi$ ground state. Conclusive experimental evidence for this assignment, however, has not been obtained to date.

Here we present the first measurement of the pure rotational spectrum of the TiF radical using millimeter/sub-mm direct absorption methods. Multiple rotational transitions were recorded for the main titanium isotopomer, ${ }^{48} \mathrm{TiF}$, each consisting of four fine structure
components, which definitively establish the ground state of the molecule as $\mathrm{X}^{4} \Phi_{\mathrm{r}}$. In addition, magnetic hyperfine splittings, resulting from the ${ }^{19} \mathrm{~F}$ nucleus, have been observed. These data have been modeled using a Hund's case (a) effective Hamiltonian, leading to the determination of rotational, fine structure, and hyperfine parameters. In this paper we present these results, interpret the constants and discuss their implications for bonding in 3 d transition metal flourides.

## II. Experimental



The pure rotational spectrum of TiF was measured using one of the quasi-optical millimeter/sub-millimeter wave direct absorption spectrometers of the Ziurys group. The major features of this instrument are outlined in Ziurys et al. [31], except that offset ellipsoidal mirrors are used as the focusing elements in this case, resulting in a different optics path. Also, a pathlength modulator is employed to improve baseline stability. The reaction chamber has a robust doubled-walled construction, which enables the melting of transition metals in a Broida-type oven attached to the cell.

The synthesis of TiF was particularly difficult because of the high melting point and reactivity of titanium. Several modifications to the oven were necessary in order to successfully vaporize this metal. First of all, crucibles constructed of boron nitride had to be used instead of the usual alumina type; liquid titanium was found to react destructively with alumina. Secondly, the oven electrodes, normally made of steel or a steel alloy, had to be constructed out of molybdenum in order to withstand the oven temperatures. Also, zirconia felt had to be placed around the top of the crucible in order to prevent liquid titanium from boiling over and onto the heating element. To create TiF, titanium vapor was first produced by the oven from heating a solid metal rod. It was then reacted with 3-5 mtorr of $\mathrm{SF}_{6}$, which was introduced into the
reaction chamber from undemeath the oven. Neither a carrier gas nor a d.c. discharge was necessary for molecular synthesis. Although titanium has several isotopes, only data for the main isotope, ${ }^{48} \mathrm{Ti}$, were recorded.

Final measurements of the rotational transitions were made from an average of one scan in increasing frequency, and the other in decreasing frequency, covering the same 5 MHz range. For the lowest frequency measurements, an average of two such scan pairs was found necessary to achieve adequate signal-to-noise ratios. In order to obtain the center frequency of each transition, Gaussian curves were fit to the line profiles. Typical linewidths ranged from 360 kHz at 142 GHz to $1,230 \mathrm{kHz}$ at 523 GHz .

## III. Results

The ground state of TiF was initially assumed to be ${ }^{4} \Phi_{\mathrm{r}}$ for the purpose of our initial spectroscopic search. In this state, spin-orbit coupling results in four fine structure levels per rotational transition, labeled by quantum number $\Omega$. Furthermore, these levels may be split again due to $\Lambda$-doubling. Although this interaction is thought to be negligible for molecules with high orbital angular momentum, lambda-doubling has been observed in pure rotational spectra of $\mathrm{CoH}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ and in the ground state of CoF , as deduced from studies of the ${ }^{3} \Phi-\mathrm{X}^{3} \Phi$ transition [ 32,33$]$. Also, magnetic hyperfine coupling due to the ${ }^{19} \mathrm{~F}$ nucleus $(\mathrm{I}=1 / 2$ ) may be present, as observed in FeF in its $\mathrm{X}^{6} \Delta_{i}$ state [23].

Searches for the rotational spectrum of TiF were aided by the optical work of Ram et al. [13], in which effective rotational constants of each fine structure component had been determined. Individual spin components were therefore readily located by scanning only a few hundred MHz , confirming the ground state assignment. Initially, the higher I transitions were
studied. Here the two higher $\Omega$ ladders $(\Omega=7 / 2$ and $9 / 2)$ were found to consist of closelyspaced doublets; their separation varied from approximately 2 MHz in the $\Omega=7 / 2$ ladder to 3 MHz in the $\Omega=9 / 2$ component. Furthermore, this splitting decreased in magnitude with increasing J, ruling out lambda-doubling interactions as their origin. In addition, transitions in the $\Omega=5 / 2$ sub-level appeared somewhat broader than expected, although the $\Omega=3 / 2$ signals had typical linewidths. The closely-spaced doublets were attributed to hyperfine interactions of the ${ }^{19} \mathrm{~F}$ nucleus, which would be expected to decrease with increasing J .

The pure rotational data recorded for TiF are presented in Table I. As the table shows, iwelve rotational transitions were measured in the frequency range $140-530 \mathrm{GHz}$. For ten of these transitions, all four fine structure components were observed with the relative intensities decreasing as the $\Omega$ value increased, definitively establishing the ground state of TiF as ${ }^{4} \Phi_{\mathrm{r}}$. The spin components also appeared to be regularly spaced as well, suggesting the spin-orbit coupling dominates the fine structure. In the higher J transitions, the fluorine hyperfine splittings were only observable in the $\Omega=9 / 2$ and $7 / 2$ ladders, although the $\Omega=5 / 2$ lines were unusually broad. As J decreased, the splitting increased such that it was eventually resolved in the $\Omega=5 / 2$ ladder at the $\mathrm{J}=18.5 \leftarrow 17.5$ transition and in the $\Omega=3 / 2$ ladder at the $\mathrm{J}=13.5 \leftarrow 12.5$ transition

Representative spectra of TiF are shown in Figures 1 and 2. In Figure 1, a spectrum of the $\Omega=3 / 2$ spin component of the $\mathrm{J}=21.5 \leftarrow 20.5$ transition near 469.7 GHz is presented. The spectrum consists of a single feature, as the hf structure is collapsed in this ladder at this high J value. In Figure 2, the $\Omega=9 / 2$ spin-orbit component of the $\mathrm{J}=20.5 \leftarrow 19.5$ transition near 456.5 GHz is shown. Here the hf doublet is clearly visible, indicated by the respective F quantum numbers. In both figures there are a few unidentified features marked by asterisks.

The regularity of the spacing of the fine structure lines in TiF is illustrated in Figure 3, which shows a stick figure of three widely separated transitions: $J=9.5 \leftarrow 8.5, \mathrm{~J}=16.5 \leftarrow 15.5$, and $\mathrm{J}=23.5 \leftarrow 22.5$. Approximate experimental intensities are displayed. Hyperfine structure is too small to be visible on this scale and thus is not shown. In all three spectra, the spin-orbit components are fairly evenly spaced, indicating that TiF closely follows a case (a) coupling scheme. The overall splitting of the fine structure components increases with J, as expected. The relative intensities of the spin components are consistent with the regular designation of the ground state.

## IV. Analysis

The pure rotational data for TiF were analyzed using a Hund's case (a) effective Hamiltonian of the form [23,34,35]:

$$
\begin{equation*}
\hat{\mathbf{H}}_{s f f}=\hat{\mathbf{H}}_{r a l}+\hat{\mathbf{H}}_{s p}+\hat{\mathbf{H}}_{s s}+\hat{\mathrm{H}}_{s o}^{(3)}+\hat{\mathbf{H}}_{h f} \tag{1}
\end{equation*}
$$

The first three terms describe molecular rotation, first order spin-orbit coupling, and spin-spin coupling respectively. The fourth expression in Eq. (1) contains the interaction characterized by the parameter $\eta$. This constant concerns the coupling of the spin-orbit and spin-spin interactions [35]:

$$
\begin{equation*}
\hat{H}_{\mathrm{so}}^{(3)}=\eta \mathrm{L}_{\mathrm{z}} \mathrm{~S}_{\mathrm{z}}\left(\mathrm{~S}_{\mathrm{z}}^{2}-\frac{3 \mathrm{~S}^{2}-1}{5}\right) \tag{2}
\end{equation*}
$$

The fifth term, $\hat{H}_{\mathrm{hf}}$ : includes the Frosch and Foley hyperfine constants $a, b$ and $c$, which take into account both $\hat{\mathrm{I}} \cdot \hat{\mathrm{L}}$ and $\hat{\mathbf{1}} \cdot \hat{\mathbf{S}}$ interactions.

The TiF data were fit using this Hamiltonian in a least squares analysis in two stages. Initially, the centroids of each hyperfine doublet in all four spin orbit components of the higher frequency transitions were analyzed to establish preliminary values of the rotational, spin-orbit, and spin-spin constants. In the process, it was found necessary to fix the spin-orbit constant, $A$, in order to achieve a satisfactory fit. (The value found by Ram et al. [13] for the spacing between the $\Omega=3 / 2$ and $5 / 2$ components was used.) The inability to fit $A$ is not surprising since TiF closely follows a case (a) coupling scheme. Once these constants were established, hyperfine interactions were then included in the analysis. Large residuals were obtained for rotational ${ }^{\prime}$ transitions higher than $\mathrm{J}=19.5 \leftarrow 18.5$ in the $\Omega=5 / 2$ spin-orbit component, because these lines had unresolved hyperfine splittings. In the final fit, these data were not included, as indicated in Table I.

The spectroscopic parameters determined for TiF are presented in Table II. The value of the rms of the millimeter-wave fit is 102 kHz , indicating the data were modeled adequately by the Hamiltonian in Eq. (1). In the process of the analysis, various higher order terms such as $\gamma_{s}$, the third order spin-rotation term [36], and $b_{s}$, the third order Fermi contact hyperfine constant [37], were included, but found not to improve the fit. Centrifugal distortion corrections to $\lambda, \eta$, and $b$ were also not required. Hence, a limited number of spectroscopic parameters were needed for the final fit, in particular for the fine structure, where $A, A_{D}, A_{H}, \lambda$ and $\eta$ were only used.

Also presented in Table II are the constants derived from the optical study of TiF [13]. The two sets of constants are in fairly good agreement, although the values of $A_{D}$ differ by about an order of magnitude. This discrepancy is expected because the optical study utilized $A_{D}$ and the spin-rotation constant, $\gamma$, whereas $A_{D}, \lambda$ and $\eta$ were used in the millimeter wave fit with no
spin-rotation parameter. $A_{D}$ and $\gamma$ are usually highly correlated parameters [39]; thus the value of $A_{D}$ will vary with that of $\gamma$.

## V. Discussion

## A. $A^{4} \Phi$ ground state for TiF

The measurement of the millimeter-wave spectrum of TiF has confirmed the ${ }^{4} \Phi_{\mathrm{r}}$ ground electronic state, as suggested by Ram et al. [13] and Boldyrev and Simons [30]. No additional features beyond the four identified were observed in this study, supporting the quartet spin multiplicity. Additionally, the half-integer values of the rotational quantum number eliminate the possibility of a ${ }^{4} \Sigma$ ground state, which is the next lowest lying term, according to theory [30]. (All attempts at fitting the data to a ${ }^{4} \Sigma$ Hamiltonian were unsuccessful.) The lack of $\Lambda$-doubling interactions in the rotational spectrum also suggests a high value of $\Lambda$. The primary electron configuration for TiF is consequently (core) $8 \sigma^{2} 3 \pi^{4} 9 \sigma^{1} 1 \delta^{1} 4 \pi^{1}$.

This study is only the second measurement of the pure rotational spectrum of a molecule in a ${ }^{4} \Phi$ ground state (and the third in any $\Phi$ state). The first such species investigated, TiCl $\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$, was also observed by millimeter-wave spectroscopy [16]. Interestingly, both these radicals were fit with relatively few (and identical) parameters, excluding hyperfine terms, despite the high values of angular momenta concerned. The only higher order constant needed in both cases was $\eta$, the spin-orbit/spin-spin interaction, which has a similar value for both TiCl (332 MHz ) and TiF ( -240 MHz ). The relatively simple analysis in both cases results from the presence of strong first order spin-orbit coupling and the lack of second-order spin-orbit effects. Second-order interactions, isoconfigurational or otherwise, result from the perturbations of nearby ${ }^{2} \Phi,{ }^{2} \Gamma,{ }^{2} \Delta,{ }^{4} \Gamma,{ }^{4} \Phi$, and ${ }^{4} \Delta$ excited states. According to Boldyrev and Simons [30], the
lowest lying excited state in both TiF (and TiCl) is ${ }^{4} \Sigma$, which would not participate in these types of perturbations. The only other state in the energy manifold calculated for $T i F$ is ${ }^{2} \Delta$, which is predicted to be $>2000 \mathrm{~cm}^{-4}$ above the ground ${ }^{4} \Phi$ state [30], and hence may be sufficiently far away in energy to have little effect.

Additional evidence for minimal second-order spin-orbit effects is the relatively small value of the spin-spin parameter in TiF $(\lambda=3681 \mathrm{MHz})$. This constant has been shown to consist of two contributions: pure spin-spin interactions and second-order spin-orbit coupling, namely $\lambda=\lambda^{5 s}+\lambda^{50}$. The second-order term is thought to dominate in heavier molecules [38]. Contributions to $\lambda^{\text {so }}$ in TiF can occur via perturbations from doublet and quartet $\Gamma, \Phi$, and $\Delta$ states, as mentioned. With the exception of the high lying $\mathrm{G}^{4} \Phi$ state, there is little definitive spectroscopic data providing the energies of these other states, except for the theoreticallypredicted ${ }^{2} \Delta$ term [30]. Therefore, it is difficult to establish which terms actually contribute to $\lambda^{50}$.

The primary second-order spin-orbit perturber in TiCl is assumed to be the $\mathrm{C}^{4} \Delta$ state, which lies $3300 \mathrm{~cm}^{-1}$ in energy above the $X^{4} \Phi$ state. (The $A$ and $B$ states are ${ }^{4} \Sigma$ and ${ }^{4} \Pi$.) It has . the electron configuration $9 \sigma^{1} 1 \delta^{1} 10 \sigma^{1}$. It is likely that a ${ }^{4} \Delta$ state also exists in the manifold of TiF. The energy of the ${ }^{4} \Delta$ state in titanium flouride in fact can be estimated from the spin-spin constant, under the assumption that $\lambda \approx \lambda^{50}$, using perturbation theory [39]. If the ${ }^{4} \Delta$ state is the dominant perturber, then

$$
\begin{equation*}
\lambda^{s 0}=\frac{\left.\left|\langle 4 \pi| a l_{+}\right| 10 \sigma\right\rangle\left.\right|^{2}}{72\left(\mathrm{E}_{\Delta}-\mathrm{E}_{\phi}\right)} \tag{3}
\end{equation*}
$$

where a is the one electron spin-orbit constant for the antibonding $4 \pi$ orbital. Evaluation of the matrix element leads to $\langle 4 \pi| a l_{+}|10 \sigma\rangle=\sqrt{6} \zeta(T i)$, assuming that the $4 \pi$ orbital is chiefly $3 \mathrm{~d}_{\pi}$ in character and the $10 \sigma$ orbital is primarily $3 \mathrm{~d}_{\boldsymbol{s}}$, centered on the titanium atom (see ref [20]). Alternatively, the $\mathrm{Ti}^{+}$spin-orbit constant may be a more appropriate choice, as suggested by recent calculations [40]. The value in $\mathrm{Ti}^{+}$is $\zeta=117 \mathrm{~cm}^{-1}$, which hardly varies from that of neutral titanium, which is $123 \mathrm{~cm}^{-1}$. Using Eq. (3), $\zeta\left(\mathrm{Ti}^{+}\right)$and the $\lambda$ value from Table II, the energy separation between the $X^{4} \Phi$ ground state and the ${ }^{4} \Delta$ state in TiF is estimated to be $\Delta E \approx$ $9300 \mathrm{~cm}^{-1}$. This value is considerably larger than the $\mathrm{C}^{4} \Delta-\mathrm{X}^{4} \Phi$ separation in TiCl , which is $3300 \mathrm{~cm}^{-1}$ [16]. Because TiF is a lighter molecule, the $\mathrm{C}^{4} \Delta-\mathrm{X}^{4} \Phi$ separation will be larger than that in TiCl , but probably not by a factor of three. Other excited electronic states are perhaps contributing to $\lambda^{\text {so }}$ to decrease its value. One such state is the isoconfigurational ${ }^{2} \Phi$ level, for which

$$
\begin{equation*}
\lambda^{\mathrm{so}}=\frac{3 A^{2}}{16\left(\mathrm{E}_{2_{\phi}}-\mathrm{E}_{\Phi_{\phi}}\right)} \tag{4}
\end{equation*}
$$

Using the $A$ value for the $X^{4} \Phi$ state, this equation suggests that the ${ }^{2} \Phi$ state lies $\sim 1760 \mathrm{~cm}^{-1}$ higher in energy above the ground state. Hence, the ${ }^{2} \Phi$ state is probably a major perturber as well.

Although lambda-doubling is thought to be negligible for $\Phi$ states, this interaction has in fact been observed in $\mathrm{CoH}\left({ }^{3} \Phi_{\mathrm{i}}\right)$ and $\operatorname{CoF}\left({ }^{3} \Phi_{i}\right)$ [32,33]. In CoH , lambda-doubling splittings on the order of $>70 \mathrm{MHz}$ were observed in LMR rotational spectra for the $\Omega=3$ spin-orbit component. This effect was unexpected, because the lambda-doubling matrix elements for $\Omega=3$ are diagonal only in $\bar{q}_{\phi}$, which is usually a small number $[32,41]$. (The $\bar{o}_{\Psi}$ constant is largest in
magnitude of the doubling parameters for triplet states). The presence of significant lambdadoubling in the $\Omega=3$ ladder suggests the presence of a nearby ${ }^{3} \Sigma$ state in CoH . The $\tilde{q}_{\phi}$ parameter derived from the analysis of the CoH spectra is $\tilde{q}_{\phi}=0.01667(24) \mathrm{MHz}[32]$. Because $\tilde{q}_{\phi}$ scales approximately as $\mathrm{B}^{6}$ [41], diatomic hydrides may be the extreme case.

The effects of $\Lambda$-doubling have also been reported for CoF, from Fourier Transform spectroscopy of the [10.3] ${ }^{3} \Phi_{i}-X^{3} \Phi_{\mathrm{i}}$ transition [19]. Splittings atuributable to this interaction were found in the $\Omega=2$ and 3 sub-bands for both electronic states. They were analyzed with a case (c) Hamiltonian, involving the effective $\Lambda$-doubling constant $q$. In the final fit, interestingly, only centrifugal distortion corrections to this parameter were used for the ground state, namely $q_{\mathrm{D}}$ and $q_{\mathrm{H}}$.

In contrast to these cobalt radicals, there was no evidence of lambda-doubling in any spin component in TiF, at least up to $\mathrm{J}=23.5$. In analogy to $\Delta$ states [41], the sub-level that should exhibit the largest effect is the $\Omega=3 / 2$ ladder, where $\tilde{n}_{\$}$ would be the major contributing term. Unfortunately, the theory of $\Lambda$-doubling for $\Phi$ states has not been examined in any detail. However, using a Van Vleck transformation [41], the $\tilde{n}_{\Phi}$ parameter can be approximated as

$$
\begin{equation*}
\tilde{n}_{\Phi} \propto \frac{B^{3} A^{3}}{(\Delta E)^{5}} \tag{5}
\end{equation*}
$$

where $B$ and $A$ are the rotational and spin-orbit constants, and $(\Delta \mathrm{E})^{5}$ are the energy differences between the $\mathrm{X}^{4} \Phi$ state and excited ${ }^{4} \Delta,{ }^{4} \Pi$, and ${ }^{4} \Sigma$ states. The obviously small value of $\tilde{n}_{\mathrm{s}}$, must arise from significant energy differences between the ground and ${ }^{4} \Pi$ and ${ }^{4} \Delta$ states. (Theory predicts the ${ }^{4} \Sigma$ state to be relatively close in energy [30].)

## B. Interpretation of Hyperfine Parameters

In this study, the ${ }^{19} \mathrm{~F}$ hyperfine splitting was modeled with $a, b$, and $(b+c)$ Frosh and Foley parameters. From these constants, the Fermi contact term $b_{F}$ and spin dipolar constant $c$ were calculated. These values are given in Table III. For comparison, hyperfine parameters for similar radicals are also listed; the sample is unfortunately limited to FeF [23] and TiN [42]. FeF and TiN have $\mathrm{X}^{6} \Delta$ and $\mathrm{X}^{2} \Sigma^{+}$ground states, respectively.

The nuclear spin orbital constant, $a$, exhibits the greatest yariations between these molecules. For example, $a$ is $\approx 67 \mathrm{MHz}$ for TiF but virtually zero for FeF. FeF has a $9 \sigma^{1} 1 \delta^{3} 4 \pi^{2} 10 \sigma^{1}$ electron configuration as opposed to $9 \sigma^{1} 1 \delta^{1} 4 \pi^{1}$ for TiF, and thus has one additional electron in an orbital with angular momentum. (The $\sigma$ orbitals do not contribute to $a$ ). At first glance, one might expect the $a$ parameter to be larger in FeF than TiF. However, the two $\pi$ electrons in FeF have their spins aligned and therefore must have equal but opposite $\hat{\mathbf{i}} \cdot \hat{\mathbf{L}}$ matrix elements so as to not violate the Pauli principle: $\left\langle\lambda_{i}^{+}\right| a_{i} I_{z} l_{i z}\left|\lambda_{i}^{+}\right\rangle=-\left\langle\lambda_{i}^{-}\right| a_{i} I_{z} l_{i}\left|\lambda_{i}^{-}\right\rangle$. Their $\hat{\mathbf{1}} \cdot \hat{\mathrm{L}}$ contributions therefore effectively cancel, in analogy to MnH [43]. The single electron in the $\pi$ orbital in TiF, in contrast, can contribute fully to the nuclear spin-orbital interaction. (The single unpaired electron in the non-bonding $\delta$ orbital in both radicals is far enough away from the fluorine nucleus such that it has a negligible effect.)

The hf constant $a$ is proportional to the inverse, cubed, of the distance $r$ between the orbiting electrons and the nucleus possessing the spin I. Hence, this constant can be used to determine the expectation value of $\sum_{n}\left\langle 1 / r_{n}^{3}\right\rangle$. For the fluorine atom, $\left\langle 1 / \mathrm{r}^{3}\right\rangle=5.9 \times 10^{31} \mathrm{~m}^{-3}$ or 8.77 in units of $a_{0}^{-3}$ [44], which primarily represents the electron-nuclear separation for a $2 p$ electron. The value for TiF is $9.07 \times 10^{29} \mathrm{~m}^{-3}$ or $0.134 \mathrm{a}_{0}^{-3}$ - over an order of magnitude
smaller (see Table III), indicating that the unpaired electrons coneributing to $a$ in this radical are located, on average, much further from the $F$ atom than a simple $2 p$ orbital. The two contributing electrons are thought to reside in $\pi$ and $\delta$ molecular orbitals, located primarily on the titanium atom. The small value derived for $\Sigma_{n}\left(1 / r_{n}^{3}\right\rangle$ supports this assumption.

Another comparison of interest are the respective Fermi contact terms. This parameter is directly proportional to the electron density at the nucleus with the spin, i.e. $b_{F} \propto\left[\psi^{2}(0)\right]$; thus, $\sigma$ molecular orbitals are thought to make the principal contribution to this parameter. For TiF, $b_{F}$ $\approx 41 \mathrm{MHz}$, while the value for FeF is 91.7 MHz (see Table III). This factor of two increase occurs because FeF has two unpaired $\sigma$ electrons, while TiF has one. TiN also has a single $\sigma$ electron, but the smaller value for the nitride compound ( $b_{F}=18.5 \mathrm{MHz}$ ) versus the fluoride in this case arises from the smaller magnetic moment of nitrogen relative to fluorine ( 0.404 vs .2 .63 Bohr magnetons [44]). In fact, normalizing the Fermi contact terms by these moments, the $\psi^{2}(0)$ value in TiN is actually larger than in TiF (see Table III). This result can be attributed to the shorter bond length in TiN relative to TiF. Consequently, the single $\sigma$ electron, located in the non-bonding $9 \mathrm{\sigma}$ orbital in both cases, can penetrate the nitrogen nucleus more effectively than that of fluorine.

Because of configuration interaction, elemental fluorine has an atomic Fermi contact term, $\mathrm{A}_{\text {iso }}(\mathrm{F})=52870 \mathrm{MHz}$ [45]. In contrast, $b_{F}$ in TiF is substantially smaller. The percent of fluorine character retained on formation of TiF is $\approx 0.08 \%$. This result is not surprising; the $\sigma$ electron in TiF is located in a non-bonding orbital primarily composed of the titanium $4 s$ orbital, in analogy to TiN [45]. The electron density at the fluorine nucleus must be minimal.

The final parameter of interest is $c$, the dipolar constant, which is an anisotropic term. It is defined as [46]:

$$
\begin{equation*}
\mathrm{c}=\frac{3 \mu_{\mathrm{o}} \mu_{1}}{1} \Sigma_{n}\left\langle\frac{3 \cos ^{2} \theta_{\mathrm{n}}-1}{r_{n}^{3}}\right\rangle \tag{6}
\end{equation*}
$$

For TiF, the value of $c$ is small and negative ( $c=-28 \mathrm{MHz}$ ), while the constant is positive and larger for $\mathrm{FeF}(c=51.7 \mathrm{MHz}$ ), and virtually zero for TiN, as shown in Table III. Because TiN has only one unpaired $\sigma$ electron, there is little to contribute to the anisotropy of the electron distribution around the nitrogen nucleus. Hence, the c parameter for TiN is very small. The differences in the magnitude of $c$ for TiF and FeF can be interpreted in terms of their proposed electron configurations. For TiF the configuration is $9 \sigma^{1} 1 \delta^{1} 4 \pi^{1}$; the $9 \sigma$ orbital must be nonbonding and composed principally of the titanium 4s atomic orbital, in analogy with TiN [45]. The only contributors to $c$ in TiF are the $1 \delta$ orbital ( $3 \mathrm{~d}_{\delta}$ orbital from the titanium atom) and the $4 \pi$ antibonding orbital, composed principally of $\mathrm{Ti} 3 \mathrm{~d}_{\pi}$ and $\mathrm{F} 2 \mathrm{p}_{\pi}$ atomic orbitals. In the case of FeF , where the principal configuration is $9 \sigma^{1} 1 \delta^{3} 4 \pi^{2} 10 \sigma^{1}$, there is an additional $4 \pi$ electron as well as one in the $10 \sigma$ antibonding orbital (a combination of the $\mathrm{F} 2 \mathrm{p}_{\mathrm{a}}$ and $\mathrm{Ti} 3 \mathrm{~d}_{\sigma}$ ). These two electrons should increase the value of c relative to that in TiF. Indeed, c in FeF is a factor of two larger in absolute magnitude. Single electron configurations consequently can explain the relative hf parameters for TiF, FeF and TiN , and lend some credence to the molecular orbital picture of these species.

## C. Trends in 3d Fluoride Species

The bonding in alkali and alkaline-earth fluorides, in general, is thought to be largely ionic [47]. Transition metal fluorides might be expected to behave similarly. Theoretical calculations of TiF predict a +0.82 e charge on the titanium atom and a dipole moment of 3 D
[30]. A large amount of ionic bonding character, however, may not apply to all of the 3d transition metals. As one moves to the right of titanium in the periodic table, the covalent character of the metal fluoride bond may be expected to increase, using simple electronegativity arguments. In fact, this increased covalency is predicted for FeF , where only $65 \%$ of the structure is predicted to be ionic [23]. A general comparison of the bonding in 3d transition metal fluorides would therefore be of great interest. Unfortunately, no comprehensive review on the transition metal fluorides exists, although 3d oxides and sulfides have been studied extensively $[20,48,49]$.

One metric by which 3d oxides (and sulfides) have been compared is via their experimentally-measured bond lengths as a function of metal atom [49]. A so-called "double hump" structure is apparent in such a plot for the oxides, as shown in Figure 4. There is an increase in bond length from V to Mn , and then another increase from Fe to Cu . This behavior is thought to occur because the $4 \pi$ antibonding orbital does not start to fill until chromium and manganese. The $\mathrm{M}-\mathrm{O}$ bond thus lengthens despite the orbital contraction that comes with increased nuclear charge [49]. This trend is repeated in the second half of the 3d row.

A plot of the bond lengths for the 3d fluorides, also presented in Figure 4, does not quite show the same trends. The most notable difference occurs in the bond lengths, which are $0.2 \AA$ larger in the fluorides relative to the corresponding oxides, with the exception of copper. This behavior suggests that the oxides have more multiple bond character than the fluorides, which routinely shortens the bond distances. Other deviations from the oxide trend for the fluorides include the increase in bond length at titanium and the lack of an increase at copper. These trends diverge because the fluorides have an extra electron relative to the oxides; at the same time, with increasing atomic number, the 3 d orbitals drop rapidly in energy relative to the 4 s ,
while the energies of the $2 p$ orbitals ( O or F ) rise [20]. From ScO to TiO , the electron configuration changes from $\sigma$ to $\sigma \delta$, i.e., the additional electron fills a nonbonding orbital; the increase in nuclear charge causes the orbitals to contract and the bond length decreases. From ScF to TiF, the configuration changes from $\sigma^{2}$ to $\sigma^{1} \delta^{1} \pi^{1}$, and the $\pi$ antibonding orbital acquires an electron, which subsequently increases the bondlength. The $\sigma^{1} \delta^{1} \pi^{3}$ configuration in TiF is generated because the 3 d orbitals have dropped sufficiently in energy at titanium such that the $4 \pi$ orbital is accessible. In addition, the 2 p orbitals in fluorine are lower in energy relative to oxygen, which in turn decreases the $4 \pi$ energy faster in the fluorides. In the oxides this orbital does not become occupied until $\mathrm{CrO}\left(\sigma^{1} \delta^{2} \pi^{1}\right)$; VO, unlike TiF, exhibits a $\sigma \delta^{2}$ configuration.

The difference in the trend at copper, on the other hand, is more problematic. Presumably the increase in bond distance for CuO results from the addition of another electron into the antibonding $4 \pi$ orbital; core contraction apparently cannot overcome this effect. The creation of CuF also adds another electron to this antibonding orbital, but in this case the shell is completed to create a ${ }^{\prime} \Sigma$ state. The filling of the $4 \pi$ shell, perhaps coupled with stronger orbital contraction in the more electronegative fluorides, results only in a slight increase in bond distance.

## IV. Conclusion

Studies of radicals in high spin states serve as tests of theory and angular momentum coupling. This investigation of TiF by pure rotational spectroscopy and subsequent spectral analysis has demonstrated that this 3 d transition metal radical can readily be modeled with a simple case (a) Hamiltonian with very few higher order terms. The regularity of the splittings of the spin-orbit components indicates that second-order effects are minimal. It is also notable that
there is no evidence of lambda-doubling in the spectra, unlike other species in $\Phi$ states. Analysis of the ${ }^{19} \mathrm{~F}$ hyperfine interactions results in parameters that are consistent with a $\sigma^{1} \delta{ }^{1} \pi^{1}$ configuration, where the $\sigma$ and $\delta$ orbitals have primarily non-bonding 3 d metal character, and the $\pi$ orbital is antibonding, formed from a linear combination of $3 \mathrm{~d}_{\pi}$ and $2 \mathrm{p}_{\pi}$ atomic orbitals. Hence, to a first approximation, the molecular orbital picture can explain the bonding in TiF, which suggests some degree of covalent behavior. Titanium fluoride was found to have a bond length $0.2 \AA$ longer than that in TiO , as is found for virtually all 3 d fluorides relative to their oxide counterparts. The bond distance in TiF lengthens because of the addition of an electron to the $4 \pi$ antibonding orbital, which does not begin to fill in the oxides until chromium. Although the 3 d fluorides have similar periodic trends to the corresponding oxides, there are subtle differences which have yet to be fully investigated.

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Table 1. Measured Rotational Transitions for TiF $\left(X^{4} \Phi_{d}\right):(y=0)^{\text {a }}$

| $J+1 \leftarrow J$ | $\mathrm{F}+1 \leftarrow \mathrm{~F}$ | $\Omega$ | $v_{\text {obs }}$ | $V_{\text {obs-calc }}$ |
| :---: | :---: | :---: | :---: | :---: |
| $6.5 \leftarrow 5.5$ | $6 \leftarrow 5$ | 1.5 | 142130.638 | -0.101 |
|  | $7 \leftarrow 6$ | 1.5 | 142125.283 | 0.093 |
|  | $6 \leftarrow 5$ | 2.5 | 143034.798 | -0.101 |
|  | $7 \leftarrow 6$ | 2.5 | 143023.571 | -0.039 |
| $9.5 \leftarrow 8.5$ | $9 \leftarrow 8$ | 1.5 | 207703.507 | -0.025 |
|  | $10 \leftarrow 9$ | 1.5 | 207701.270 | 0.003 |
|  | $9 \leftarrow 8$ | 2.5 | 209019.847 | 0.007 |
|  | $10 \leftarrow 9$ | 2.5 | 209014.655 | -0.074 |
|  | $9 \leftarrow 8$ | 3.5 | 210369.579 | -0.082 |
|  | $10 \leftarrow 9$ | 3.5 | 210361.072 | -0.082 |
|  | $9 \leftarrow 8$ | 4.5 | 211769.550 | 0.073 |
|  | $10 \leftarrow 9$ | 4.5 | 211757.027 | 0.065 |
| $10.5 \leftarrow 9.5$ | $10 \leftarrow 9$ | 1.5 | 229556.230 | -0.012 |
|  | $11 \leftarrow 10$ | 1.5 | 229554.452 | -0.041 |
|  | $10 \leftarrow 9$ | 2.5 | 231009.810 | 0.004 |
|  | $11 \leftarrow 10$ | 2.5 | 231005.651 | -0.015 |
|  | $10 \leftarrow 9$ | 3.5 | 232500.158 | -0.095 |
|  | $11 \leftarrow 10$ | 3.5 | 232493.213 | -0.058 |
|  | $10 \leftarrow 9$ | 4.5 | 234045.720 | -0.014 |
|  | $11 \leftarrow 10$ | 4.5 | 234035.453 | 0.045 |
| $12.5 \leftarrow 11.5$ | $12 \leftarrow 11$ | 1.5 | 273252.290 | 0.074 |
|  | $13 \leftarrow 12$ | 1.5 | 273251.054 | -0.094 |
|  | $12 \leftarrow 11$ | 2.5 | 274979.759 | 0.095 |
|  | $13 \leftarrow 12$ | 2.5 | 274976.791 | -0.017 |
|  | $12 \leftarrow 11$ | 3.5 | 276750.771 | 0.058 |
|  | $13 \leftarrow 12$ | 3.5 | 276745.647 | -0.101 |
|  | $12 \leftarrow 11$ | 4.5 | 278586.761 | -0.043 |
|  | $13 \leftarrow 12$ | 4.5 | 278579.477 | 0.104 |
| $13.5 \leftarrow 12.5$ | $13 \leftarrow 12$ | 1.5 | 295094.922 | 0.080 |
|  | $14 \leftarrow 13$ | 1.5 | 295093.981 | -0.025 |
|  | $13 \leftarrow 12$ | 2.5 | 296958.889 | 0.054 |
|  | $14 \leftarrow 13$ | 2.5 | 296956.403 | -0.013 |
|  | $13 \leftarrow 12$ | 3.5 | 298869.789 | 0.024 |
|  | $14 \leftarrow 13$ | 3.5 | 298865.325 | -0.162 |
|  | $13 \leftarrow 12$ | 4.5 | 300850.750 | 0.060 |
|  | $14 \leftarrow 13$ | 4.5 | 300844.138 | -0.107 |
| $16.5 \leftarrow 15.5$ | $16 \leftarrow 15$ | 1.5 | 360597.403 | -0.171 |
|  | $17 \leftarrow 16$ | 1.5 | 360597.403 | 0.208 |
|  | $16 \leftarrow 15$ | 2.5 | 362869.367 | 0.146 |
|  | $17 \leftarrow 16$ | 2.5 | 362867.599 | -0.068 |
|  | $16 \leftarrow 15$ | 3.5 | 365197.688 | 0.010 |
|  | $17 \leftarrow 16$ | 3.5 | 365194.829 | 0.068 |

Table I. cont'd.

| $\mathrm{J}+1 \leftarrow \mathrm{~J}$ | $\mathrm{F}+1 \leftarrow \mathrm{~F}$ | $\Omega$ | $V_{\text {obs }}$ | $V_{\text {obs-calc }}$ |
| :---: | :---: | :---: | :---: | :---: |
| $16.5 \leftarrow 15.5$ | $16 \leftarrow 15$ | 4.5 | 367610.742 | 0.014 |
|  | $17 \leftarrow 16$ | 4.5 | 367606.330 | 0.093 |
| $17.5 \leftarrow 16.5$ | $17 \leftarrow 16$ | 1.5 | 382422.304 | -0.116 |
|  | $18 \leftarrow 17$ | 1.5 | 382422.304 | 0.161 |
|  | $17 \leftarrow 16$ | 2.5 | 384829.420 | 0.222 |
|  | $18 \leftarrow 17$ | 2.5 | 384827.632 | -0.206 |
|  | $17 \leftarrow 16$ | 4.5 | 389852.043 | -0.164 |
|  | $18 \leftarrow 17$ | 4.5 | 389848.279 | 0.123 |
| $18.5 \leftarrow 17.5$ | $18 \leftarrow 17$ | 1.5 | 404241.985 | -0.077 |
|  | $19 \leftarrow 18$ | 1.5 | 404241.985 | 0.114 |
|  | $18 \leftarrow 17$ | 2.5 | 406783.622 | 0.070 |
|  | $19 \leftarrow 18$ | 2.5 | 406782.206 | -0.149 |
|  | $18 \leftarrow 17$ | 3.5 | 409388.332 | 0.035 |
|  | $19 \leftarrow 18$ | 3.5 | 409385.767 | -0.176 |
|  | $18 \leftarrow 17$ | 4.5 | 412087.036 | -0.070 |
|  | $19 \leftarrow 18$ | 4.5 | 412083.552 | 0.127 |
| $20.5 \leftarrow 19.5$ | $20 \leftarrow 19$ | 1.5 | 447864.621 | 0.099 |
|  | $21 \leftarrow 20$ | 1.5 | 447864.621 | 0.157 |
|  | $20 \leftarrow 19$ | 2.5 | $450673.700^{\text {b }}$ | -0.381 |
|  | $21 \leftarrow 20$ | 2.5 | $450673.700^{\text {b }}$ | 0.559 |
|  | $20 \leftarrow 19$ | 3.5 | 453553.392 | 0.183 |
|  | $21 \leftarrow 20$ | 3.5 | 453551.256 | -0.005 |
|  | $20 \leftarrow 19$ | 4.5 | 456535.547 | -0.088 |
|  | $21 \leftarrow 20$ | 4.5 | 456532.474 | -0.064 |
| $21.5 \leftarrow 20.5$ | $21 \leftarrow 20$ | 1.5 | 469666.659 | -0.075 |
|  | $22 \leftarrow 21$ | 1.5 | 469666.659 | -0.070 |
|  | $21 \leftarrow 20$ | 2.5 | $472609.283{ }^{\text {b }}$ | -0:321 |
|  | $22 \leftarrow 21$ | 2.5 | $472609.283{ }^{\text {b }}$ | 0.517 |
|  | $21 \leftarrow 20$ | 3.5 | 475625.367 | 0.221 |
|  | $22 \leftarrow 21$ | 3.5 | 475623.369 | 0.009 |
|  | $21 \leftarrow 20$ | 4.5 | 478748.469 | -0.036 |
|  | $22 \leftarrow 21$ | 4.5 | 478745.702 | 0.061 |
| $22.5 \leftarrow 21.5$ | $22 \leftarrow 21$ | 1.5 | 491462.521 | -0.009 |
|  | $23 \leftarrow 22$ | 1.5 | 491462.521 | -0.050 |
|  | $22 \leftarrow 21$ | 2.5 | $494537.916^{\text {b }}$ | -0.282 |
|  | $23 \leftarrow 22$ | 2.5 | $494537.916^{\text {b }}$ | 0.468 |
|  | $22 \leftarrow 21$ | 3.5 | 497689.716 | 0.114 |
|  | $23 \leftarrow 22$ | 3.5 | 497687.828 | -0.129 |
|  | $22 \leftarrow 21$ | 4.5 | 500953.309 | 0.032 |
|  | $23 \leftarrow 22$ | 4.5 | 500950.642 | 0.026 |
| $23.5 \leftarrow 22.5$ | $23 \leftarrow 22$ | 1.5 | 513251.593 | -0.014 |
|  | $24 \leftarrow 23$ | 1.5 | 513251.593 | -0.095 |

Table I. cont'd.

| $\mathrm{J}+1 \leftarrow \mathrm{~J}$ | $\mathrm{~F}+1 \leftarrow \mathrm{~F}$ | $\Omega$ | $V_{\text {obs }}$ | $V_{\text {obs-calc }}$ |
| :---: | :---: | :---: | :---: | ---: |
|  |  |  |  |  |
| $23.5 \leftarrow 22.5$ | $23 \leftarrow 22$ | 2.5 | $516459.256^{\mathrm{b}}$ | -0.281 |
|  | $24 \leftarrow 23$ | 2.5 | $516459.256^{\mathrm{b}}$ | 0.391 |
|  | $23 \leftarrow 22$ | 3.5 | 519746.260 | 0.030 |
|  | $24 \leftarrow 23$ | 3.5 | 519744.630 | -0.078 |
|  | $23 \leftarrow 22$ | 4.5 | 523149.537 | -0.038 |
|  | $24 \leftarrow 23$ | 4.5 | 523147.015 | -0.078 |

a) $\ln \mathrm{MHz}$
b) Blended lines, not included in the fit.

Table 11. Spectroscopic Parameters for $\left.\operatorname{TiF}\left(X^{4} \Phi_{r}\right): v=0^{\text {i }}\right)$

| Parameter | Millimeter-Wave | Optical ${ }^{\text {b }}$ |
| :---: | :---: | :---: |
| B | $11040.0976(29)$ | $11037.5(2.4)$ |
| D | $0.0140322(38)$ | $0.0121(20)$ |
| A | $\left.1018000^{\mathrm{c}}\right)$ | 1018000 |
| $\mathrm{~A}_{\mathrm{D}}$ | $-3.45663(84)$ | 22.9 |
| $\mathrm{~A}_{\mathrm{H}}$ | $3.22(10) \times 10^{-5}$ | - |
| $\gamma$ | - | $10400(1200)$ |
| $\lambda$ | $3681.2(7.0)$ |  |
| $\eta$ | $-240.0(4.0)$ |  |
| a | $67.4(1.1)$ |  |
| b | $50(13)$ |  |
| $\mathrm{b}+\mathrm{c}$ | $21.7(5.0)$ |  |
| ms | 0.102 |  |

a) $\ln \mathrm{MHz}$ e errors are $3 \sigma$ and apply to the lasi quoted decimal places.
b) From ref [13]. Values originally quoted in $\mathrm{cm}^{-1}$.
c) Held fixed (see text).

Table ILI. Hyperfine Parameters for TiF and Related Species ${ }^{\text {a }}$

| Molecule | a | b | c | $\mathrm{b}_{5}$ | $\psi^{2}(0)^{\text {b }}$ | $\sum_{n}\left(1 / r_{n}^{3}\right)^{b)}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| TiF $\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$ | 67.4(1.1) | 50(13) | -28(14) | 41(14) | 0.0101 | 0.134 |
| $\operatorname{TiN}\left(\mathrm{X}^{2} \Sigma^{+}\right)^{\text {c }}$ |  | 18.535(14) | $0.166(21)$ | 18.480(9) | 0.057261 |  |
| $\mathrm{FeF}\left(\mathrm{X}^{6} \Delta_{i}\right)^{\text {d }}$ ) | -0.45 ${ }^{\text {e }}$ | $74.5(3.5)$ | 51.7(3.5) | 91.7(3.7) | 0.0218 | 0.00090 |

a) $\ln \mathrm{MHz}$.
b) In units of $a_{0}{ }^{-3}$.
c) Ref. 42
d) Ref. 23
e) Fixed value.

## Figure Captions

Figure 1. Spectrum of the $J=21.5 \leftarrow 20.5$ rotational transition of $T i F\left(X^{4} \Phi_{8}\right)$ in its lowest spin component, $\Omega=3 / 2$, observed near 469.7 GHz . The weaker lines marked by an asterisk are unidentified. Hyperfine splittings, which arise from interactions with the ${ }^{19} \mathrm{~F}$ nuclear spin, are not apparent in these data and only appear at much lower J transitions. This spectrum is a single, 100 MHz scan obtained in approximately one minute.
Figure 2. Spectrum of the $\mathrm{J}=20.5 \leftarrow 19.5$ rotational transition of $\mathrm{TiF}\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$ in the $\Omega=9 / 2$ spin component recorded near 456 GHz . Here the ${ }^{19} \mathrm{~F}$ hf interactions are clearly visible, splitting the transition into closely-spaced doublets, which are labeled by quantum number $F$. The weak feature marked by an asterisk is unidentified. This spectra is a single 100 MHz scan, lasting one minute in duration.

Figure 3. A stick diagram illustrating the progression of the four spin components in TiF, over a wide range of frequency. The approximate relative intensities are shown, and each plot covers ~ 11 GHz . The separation of spin components increases with increasing J - almost a factor of two from the $\mathrm{J}=9.5 \leftarrow 8.5$ to the $\mathrm{J}=23.5 \leftarrow 22.5$ transitions. However, all four spin components are evenly spaced, even at high J , indicating strong spin-orbit coupling in TiF .

Figure 4. A graph showing the periodic trends in bond lengths for the 3 d transition metal oxides vs. the fluorides. The oxides exhibit the characteristic "double hump" structure in this plot, i.e. the bond lengths increase from V to Mn and from Fe to Cu , indicating the competition between addition of antibonding electrons vs. core contraction. The fluorides show a similar trend, but with variations at titanium and copper. The increase in bond length at TiF likely results from the addition of an electron to the $4 \pi$ antibonding orbital, which does not start to fill in the oxides until chromium.

Spectrum of TiF $\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right): \Omega=3 / 2$


Fir 1




## APPENDIX J

MOLECULES IN HIGH SPIN STATES II: THE PURE ROTATIONAL SPECTRUM OF $\operatorname{MnF}\left(\mathrm{X}^{7} \Sigma^{+}\right)$
P. M. Sheridan and L. M. Ziurys, Chem. Phys. Lett. accepted.

## Molecules in High Spin States II:

# The Pure Rotational Spectrum of $\mathrm{MnF}\left(\mathrm{X}^{7} \Sigma^{+}\right)$ 

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[^10]
#### Abstract

The pure rotational spectrum of MnF has been measured in its $\mathrm{X}^{7} \Sigma^{+}$ground state using millimeter/sub-millimeter direct absorption methods. Five and six rotational transitions, respectively, were recorded for this radical in its $v=0$ and $v=1$ states in the range $338-630$ GHz . MnF was created from $\mathrm{SF}_{6}$ and manganese vapor, produced in a Broida-type oven. The species exhibited a complex pattern where the fine and ${ }^{55} \mathrm{Mn}$ and ${ }^{19} \mathrm{~F}$ hyperfine structures are intermixed. Rotational, spin-rotation, spin-spin and hyperfine parameters have been determined for MnF. These constants have been interpreted in terms of bonding and electronic structure in metal fluorides.


## I. Introduction

The spectra of even small 3d transition metal compounds are usually quite complex. The complexity arises from the presence of 3d electrons, which give rise to a multitude of closely-spaced electronic states [1]. Determination of the ground electronic term of these molecules is consequently quite problematic. For example, the ground state of TiF over the years has been assigned as ${ }^{4} \Sigma[2],{ }^{2} \Delta[3]$, and ${ }^{4} \Phi[4,5]$. The ground state of $F e N$ has still yet to be conclusively determined, although it is most likely to be ${ }^{2} \Delta$ or $\Pi$ [6].

Perhaps some of the most complicated spectra of molecules containing 3d transition metals are those with manganese. The element has a $4 s^{2} 3 d^{5}$ electron configuration, and hence a half-filled 3d shell. Therefore, extremely high multiplicities and orbital angular momentum values can be generated in manganese compounds, as evidenced by even the simplest of these species. $\mathrm{MnH}[7,8,9]$. Measurements of the $\mathrm{A}^{7} \Pi \rightarrow \mathrm{X}^{7} \Sigma^{+}$transition of this radical have necessitated a detailed analysis, which has been additionally complicated by the presence of the two nuclear spins of ${ }^{55} \mathrm{Mn}(\mathrm{I}=5 / 2)$ and ${ }^{1} \mathrm{H}(\mathrm{I}=1 / 2)[7,8]$. The hyperfine interactions in MnH have in fact been found to be so substantial that they cause mixing of the seven spin components, destroying the "goodness" of the J quantum number [9]. Pure rotational spectra have also been recorded for MnO [10] and MnS [11], as well, in their $\mathrm{X}^{6} \Sigma^{+}$ground states. In both cases, higher order fine and hyperfine constants were found necessary to fully analyze these problematic data sets. In addition, various electronic bands of MnCl have been recorded [12]; again, assignment of the transitions has proved to be difficult.

Another manganese-bearing species of interest is MnF . The earliest spectroscopic observation of this radical occurred in 1939, where two band systems were recorded [13]. More recent investigations occurred in 1978, when matrix isolation studies resulted in the
determination of $\mathrm{A}_{\text {iso }}$ and $\mathrm{A}_{\text {dip }}$ hyperfine parameters [14]. Additional gas-phase work has been conducted by Launila, Simard and collaborators (e.g. [15, 16]), who recorded the $A^{7} \Pi-X^{7} \Sigma^{+}$, $c^{5} \Sigma^{+}-a^{5} \Sigma^{+}, d^{5} \Pi-a^{5} \Sigma^{+}$, and $b^{5} \Pi-a^{5} \Sigma^{+}$transitions using LIF. For these works, MnF was created in a supersonic jet using laser ablation techniques. These studies verified the ground state of MnF to be $\mathrm{X}^{7} \Sigma^{+}$, and established a rotational constant of $0.35173 \mathrm{~cm}^{-1}$. (A more complete set of spectroscopic parameters was determined for the $A^{7} \Pi$ state.) Ab initio calculations have not been carried out for MnF to date.

As part of our interest in investigating molecules in high spin states, as well as studying trends in 3 d transition metal fluorides, we have recorded the pure rotational spectrum of MnF $\left(X^{7} \Sigma^{+}\right)$in its $v=0$ and $v=1$ states. Because of the presence of two nuclear spins in this radical, as well as six unpaired electrons, the observed spectra were expected to be complicated; this situation was exacerbated by the relatively small magnitude of the spin interactions, which meant that the hyperfine components associated with each spin state could not be easily distinguished. However, the spectral pattern could be sufficiently resolved such that rotational, fine structure, and hyperfine constants were obtained. Here we present these data and their analysis, and discuss the derived parameters in terms of bonding in manganese compounds and in 3d transition metal fluorides.

## 2. Experimental

The pure rotational spectrum of MnF was measured using one of the direct absorption millimeter/sub-millimeter-wave spectrometers of the Ziurys lab [17]. Briefly, the instrument consists of three basic parts: a radiation source composed of Gunn oscillators and Schottky diode multipliers, a high temperature reaction chamber containing a Broida-type oven, and an InSb bolometer detector. Offset ellipsoidal mirrors are used as the focusing elements and a
pathlength modulator is employed for baseline smoothing. The radiation is FM modulated at $\pm$ 25 kHz and detected at 2 f by a lock-in-amplifier.

The MnF radical was synthesized by the reaction of Mn vapor, produced in a Broidatype oven, with approximately 20 mtorr of $\mathrm{SF}_{6}$ gas. The reactant gas was added to the reaction cell from undemeath the oven. Production of the MnF radical was not found to increase upon addition of a carrier gas such as Ar or by employing a d.c. discharge; hence, neither was used. During the reaction, no chemiluminescence was observed.

Final frequency measurements of each rotational transition were obtained by averaging an even number of scan pairs 5 MHz wide, one taken in increasing and the other in decreasing frequency. Gaussian line shapes were then fit to these averages. For the lower frequency transitions and those in the $v=1$ state, up to 6 such pairs were found to be necessary to achieve an adequate signal-to-noise ratio. Typical line widths ranged from 850 kHz at 338 GHz to $1,700 \mathrm{kHz}$ at 628 GHz . Many features appeared to be broader, a result of line blending.

## 3. Results

Manganese has a spin of $\mathrm{I}_{1}=5 / 2$, and ${ }^{19} \mathrm{~F}$ has a spin of $\mathrm{I}_{2}=1 / 2$. Consequently, to a first approximation, every rotational transition in $\mathrm{MnF}\left(\mathrm{X}^{7} \Sigma^{+}\right)$is split into $(2 \mathrm{~S}+1)\left(2 \mathrm{I}_{1}+1\right)\left(2 \mathrm{I}_{2}+1\right)=$ 84 separate fine structure/hyperfine components. However, the spin interactions are sufficiently small in manganese fluoride such that the hyperfine transitions originating in each separate spin component overlap. Hence, one continuous spectrum of numerous congested and partially blended transitions results. Such a pattern is not found in either $\mathrm{MnO}\left(\mathrm{X}^{6} \mathrm{\Sigma}^{+}\right)$or MnS $\left(X^{6} \Sigma^{+}\right) . \ln$ these cases, the spin components are sufficiently spaced in frequency that their respective hyperfine patterns are clearly separated. Furthermore, both these molecules only have a single nuclear spin.

Typical spectra showing the convoluted pattem in MnF in its $\mathrm{v}=0$ state are presented in Figure 1. Here the $\mathrm{N}=17 \leftarrow 16,19 \leftarrow 18$, and $23 \leftarrow 22$ rotational transitions are displayed. A clear fine structure and/or hyperfine pattern are not apparent in these data. The 84 individual transitions are compressed into a 100 MHz range, and hence there are many blended lines, further confused because of the second derivative line shapes. Several individual features are present in these data, however, especially at the extrema of each rotational hypermultiplet. (The largest hyperfine splittings are expected for the $\mathrm{F}_{1}: \mathrm{J}=\mathrm{N}+3$ and $\mathrm{F}_{7}: \mathrm{J}=\mathrm{N}-3$ spin components [9], which are at the lowest and highest frequency end of a given transition.) Other individual transitions are also discernable midway through the morass of lines. Several repeating features are traced by dashed lines in the figure in successive spectra. The $\mathrm{v}=1$ data are very similar in appearance.

Transition frequencies established from these spectra are presented in Table 1. As the table illustrates, five transitions were measured for MnF in the $\mathrm{v}=0$ state. Listed here are the frequencies of all spectra lines that could be resolved in the complex pattern, a total of 319 features considering all transitions. Some lines have been identified as a blend of multiple components arising from the nuclear spins; hence, the frequency appears more than once in the table. In addition, six transitions were measured for MnF in the $\mathrm{v}=1$ vibrational state. The N $=18 \leftarrow 17,19 \leftarrow 18,22 \leftarrow 21,23 \leftarrow 22,24 \leftarrow 23$, and $30 \leftarrow 29$ transitions were recorded, which lie in the frequency range $377-630 \mathrm{GHz}$. A total of 241 individual features were measured for the $v=1$ state. This data set is available on request from the authors.

## 4. Analysis

The MnF data were fit to the following effective Hamiltonian, using a case $b_{\beta J}$ basis set
[18]:

$$
\begin{equation*}
\hat{H}_{\mathrm{eff}}=\hat{\mathrm{I}}_{\mathrm{rot}}+\hat{\mathrm{H}}_{\mathrm{st}}+\hat{\mathrm{H}}_{\mathrm{ss}}+\hat{\mathrm{H}}_{\mathrm{hff(mm)}}+\hat{\mathrm{H}}_{\mathrm{hf(F)}} \tag{1}
\end{equation*}
$$

The terms in Eq. (1) describe rotational motion, spin-rotation and spin-spin fine structure and magnetic hyperfine interactions for the manganese and fluorine nuclei.

Due to the highly convoluted nature of the fine and hyperfine structure within each rotational transition of MnF , the spectral analysis was conducted in several stages. First, five clearly resolved features appearing on the high frequency side of the rotational transitions in the $v=0$ level were fit to obtain preliminary values of $B, D$, the spin-fpin constant $\lambda$, the spinrotation constant $\gamma$, and the Mn hyperfine constants, $b_{F}$ and $c$. From this initial fit, $\gamma$ was found to have a positive value and $\lambda$ a negative one, consistent with the signs of those constants obtained for $\mathrm{MnH}[7,8,9]$, lending some legitimacy to the analysis. Based on these preliminary parameters, the complete MnF spectrum was then repredicted. A simulation program was helpful in this regard. It was then immediately obvious that ${ }^{19} \mathrm{~F}$ hyperfine interactions had to be included in the analysis. (The strengths of some of the lines were clearly under-predicted and obvious doublets in the observed spectra were calculated to be single features.) Employing fluorine hf parameters eliminated many of these discrepancies, although it was found necessary to fix the dipolar constant of ${ }^{19} \mathrm{~F}$ to the value given in the matrix studies [14]. The data fit was again reiterated several times to "fine tune" the observed line intensities and account for as many features in the experimental data as possible. For comparison, simulated spectra were generated.

The final results of the analysis are illustrated in Figure 2. Here the observed spectrum of the $N=18 \leftarrow 17$ transition $(v=0)$ near 380 GHz is presented in the top panel. In the lower panel, the simulated spectrum is shown, which is based on the constants established in the final fit, including relative intensities. All strong individual lines in these data are well reproduced
by the simulation, as are many of the weaker features. (The simulation accounts for the second derivative spectrum and hence enables elimination of "ghost" features.) Interestingly, the best fit included transitions with $\Delta J$ changing by $\pm 2$ and greater, as well as those with $\Delta F_{1}= \pm 2$. These unusual transitions account for $\sim 10 \%$ of the observed lines. They arise from hyperfine mixing, which results in the breakdown of J as a good quantum number. Such effects were also noticed in $\mathrm{MnH}[7,8,9]$, another case where the hyperfine interactions were comparable to the spin splittings. The $v=1$ data set was analyzed in an identical manner.

The spectroscopic parameters obtained for $\mathrm{MnF}(\mathrm{v}=0$ and $\mathrm{v}=1)$ are presented in Table 2. As shown in the table, in the final fit the dipolar hf constant for the ${ }^{19} \mathrm{~F}$ nucleus had to be fixed, as mentioned previously. All other spectroscopic constants are well determined, and the rms of the fits are $204 \mathrm{kHz}(\mathrm{v}=0)$ and $244 \mathrm{kHz}(\mathrm{v}=1)$. Curiously, the only spin parameters that were needed in the analysis were $\gamma$, the spin-rotation constant, and $\lambda$, the spin-spin parameter, and $\lambda_{\mathrm{D}}$. Centrifugal distortion corrections to $\gamma$, as well as higher order terms such as $\theta, \gamma_{s}$, and $b_{s}$, were used in the initial analyses but could not be defined. In contrast, $\gamma_{\mathrm{D}}, \gamma_{\mathrm{s}}, \theta$, and $\mathrm{b}_{\mathrm{F}_{\mathrm{D}}}$ were all found to be necessary to fit $\mathrm{MnS}[11]$ and $\mathrm{MnO}[10]$ in their $\mathrm{X}^{6} \Sigma^{+}$states.

One major difference between MnF and these other manganese compounds is the magnitude of the fine structure interactions, which is substantially smaller in the fluoride. For example, the spin-spin constant is near 10 GHz in MnS and 17 GHz in MnO , while in MnF it is -136.5 MHz - two orders of magnitude smaller. The spin-rotation constant is smaller by a factor of 4 in the fluoride relative to the sulfide and oxide as well, which both have $\gamma \simeq-71$ MHz [10,11]. Hence, higher order terms may be sufficiently small such that they are not needed for MnF . It also may be difficult to determine values of these higher-order constants as well, given the congested spectra. It is interesting to note that the electric quadrupole constant
eqQ for the ${ }^{55} \mathrm{Mn}$ nucleus was not defined in the MnF analysis as well; again, this parameter was determined for both MnO and MnS . For the latter species, however, lower N rotational transitions were recorded, and quadrupole splittings decrease with increasing N. Moreover, these spectra were far less congested.

Also included in Table 2 are the constants determined for MnF from previous work. The data set is small: it includes a gas-phase estimate of the rotational constant $(v=0)$ from optical spectra [15], as well as hf parameters from matrix ESR studies [14]. The values for the rotational constant $B$ are in reasonable agreement. The hf parameters $b_{F}$ and $c$ compare satisfactorily, as well, for both ${ }^{19} \mathrm{~F}$ and ${ }^{55} \mathrm{Mn}$ nuclei ( $\left({ }^{(19} \mathrm{F}\right)$ was fixed, as mentioned). It is also not clear whether the uncertainties of the matrix values quoted from ref. 14 are one or three standard deviations. If they are only $1 \sigma$, then the gas-phase and matrix isolation constants are in complete agreement. If the quoted uncertainties are $3 \sigma$, then the gas-phase parameters are systematically smaller than the matrix values for the ${ }^{55} \mathrm{Mn}$ nucleus. This systematic difference was found in MnH , where the Fermi contact term for the ${ }^{55} \mathrm{Mn}$ nucleus was $11 \%$ smaller, based on the gas-phase study. This effect was attributed to a large matrix shift.

## 5. Discussion

## i) Minimal Fine Structure Interactions in MnF

In comparison to molecules in equally high spin states such as $\mathrm{MnS}\left({ }^{6} \Sigma^{+}\right)$and MnO ( ${ }^{6} \Sigma^{+}$), the spin-spin constant determined for MnF is remarkably small. A similar situation is found in $\mathrm{MnH}\left(\mathrm{X}^{7} \Sigma^{+}\right)$, where $\lambda=-97 \mathrm{MHz}[9]$, comparable to that found for MnF . The small value of $\lambda$ can be understood in terms of second-order contributions to this parameter. The magnitude of $\lambda$ is determined by the pure microscopic spin-spin interactions, and a secondorder spin-orbit perturbation [19], i.e.

$$
\begin{equation*}
\lambda=\lambda^{s s}+\lambda^{s 0} \tag{2}
\end{equation*}
$$

The latter effect is thought to dominate in heavier molecules, and certainly those containing a 3d transition metal. The spin-orbit contribution arises from perturbations of nearby excited states, following the selection rules $\Delta S=0, \pm 1 ; \Delta \Omega=0 ; \Sigma^{ \pm} \leftrightarrow \Sigma^{\mp}$ [19]. Consequently, a ${ }^{7} \Sigma^{+}$ state can only interact with ${ }^{2} \Sigma^{-},{ }^{5} \Sigma^{-}, 5$, and ${ }^{7} \Pi$ states for this type of coupling.

Little is quantitatively known about the excited electronic states of MnF , other than the $A^{7} \Pi$ state lies $28,000 \mathrm{~cm}^{-1}$ higher in energy above the $\mathrm{X}^{7} \Sigma^{+}$state [ 15 ]. There is some indication that the $a^{5} \Sigma^{+}$may lie lower in energy than the $A$ state $[20]$, and the $b^{5} \Pi$ term as well $[16,9]$. However, no theoretical calculation exists for MnF to verify these energies. The $a \Sigma^{+}$state has positive Kronig symmetry and hence cannot interact with the $\mathrm{X}^{7} \Sigma^{+}$via second-order spin-orbit coupling. The $b^{5} \Pi$ term is also eliminated as a possible perturber because it arises from a $3 d^{6}$ electron configuration, as opposed to $3 \mathrm{~d}^{5}$. The only remaining perturber is the $A^{7} \Pi$ state. The second order spin-orbit interaction for MnF is therefore well approximated by the expression:

$$
\begin{equation*}
\lambda^{\mathrm{so}} \cong \frac{\left.\left|\left\langle\mathrm{~A}^{7} \Pi\right| \hat{\mathrm{H}}_{\mathrm{so}}\right| \mathrm{X}^{7} \Sigma^{+}\right\rangle\left.\right|^{2}}{\mathrm{E}\left(\mathrm{X}^{7} \Sigma^{+}\right)-\mathrm{E}\left(\mathrm{~A}^{7} \mathrm{I}\right)} \tag{3}
\end{equation*}
$$

The structure of MnF is likely to be highly ionic. Thus, the $\mathrm{X}^{7} \Sigma$ and $\mathrm{A}^{7} \Pi$ states can be approximated as $\mathrm{Mn}^{+}\left(3 \mathrm{~d}^{5} 4 \mathrm{~s}^{1}\right) \mathrm{F}^{-}\left(2 p^{6}\right)$ and $\mathrm{Mn}^{+}\left(3 d^{5} 4 p^{1}\right) \mathrm{F}^{-}\left(2 p^{6}\right) . \hat{H}_{\text {so }}$ is a one electron operator and diagonal in $\ell$. Consequently, at least to first order, the $X^{7} \Sigma$ and $A^{7} \Pi$ states cannot connect via this interaction. The numerator in the above expression must be negligible. The large energy difference in the denominator $\left(28,000 \mathrm{~cm}^{-1}\right)$ also reduces the value of $\lambda^{\text {so }}$.

The magnitude of the spin-rotation constant in MnF is also small ( $\gamma=16.7152 \mathrm{MHz}$ ). Again, there are two main contributions to this parameter: microscopic electron spin-nuclear
rotation coupling and a second-order spin-orbit effect [19]. The latter interaction involves the cross-term $\hat{H}_{50} \times \hat{H}_{\text {rot }}$ and follows the selection rule $\Delta S=0$; hence, once again, the $A^{7} \Pi$ state is the main perturber. As previously discussed, $\hat{H}_{\text {so }}$ cannot readily connect these two states; they have a large energy separation as well. The second-order contribution to $\gamma$ is therefore minimal. In comparison, the spin-rotation constant in MnH is significantly larger $(\gamma=909.6$ MHz [9]). This increase reflecis the larger rotational constant in the hydride, which enters into $\gamma$ through $\hat{H}_{\text {rot }}$.
ii) Comparison of Hyperfine Parameters

Trends across the periodic table for 3 d metal oxides have been examined in detail [e.g. $1,21,22]$, including numerous calculations concerning the bonding and degree of hybridization of molecular orbitals. For the fluoride analogs, such studies are far more incomplete. On the other hand, such trends can be examined in 3d fluorides by comparison of ${ }^{19} \mathrm{~F}$ magnetic hf constants, which give insight into the nature of the molecular orbitals of the species.

Unfortunately, such hf parameters have only been determined for a few of the 3d fluorides; these values are given in Table 3 for TiF, FeF and MnF . (NiF is not included in this group because only $h=[a+(b+c) / 2]$ could be established [23].)

As shown in Table 3, the Fermi contact term $b_{F}$ for the fluoride nucleus for all three species is relatively small, indicating that the unpaired electrons from s atomic orbitals in these radicals are primarily located on the metal atom. This result is not surprising because these species are predominantly ionic, and hence exhibit an $\mathrm{M}^{+} \mathrm{F}^{-}$structure. Thus, there are no unpaired electrons present directly on the ${ }^{19} \mathrm{~F}$ nucleus in this picture. The differences in the magnitudes of the $b_{F}$ parameters in these species, however, can be best rationalized in terms of their proposed electron configuration, shown in Table 3. The possible contributing electrons to
the Fermi contact interaction are the $9 \sigma$ and $10 \sigma$ orbitals. The $9 \sigma$ is considered to be primarily non-bonding, hence it resides exclusively on the metal atom [21]. The $10 \sigma$ orbital is antibonding and likely consists of some combination of fluorine $p_{0}$ and metal sd $\alpha_{\sigma}$ atomic character. It is likely that the electron in the $10 \sigma$ orbital makes the primary contribution to $b_{F}$ in MnF and FeF ; their constants are closer in magnitude. TiF has no electrons in the $10 \sigma$ orbital; consequently, the value of $b_{F}$ in this species is smaller.

The dipolar constant $c$ in all three species is also small in magnitude. Again, because the unpaired electrons are primarily located on the metal atom, their contribution to $c$ is negligible. The dipolar constant in FeF is significantly larger than in TiF; this increase likely arises because of occupation of the $10 \sigma$ orbital.

The ${ }^{19} \mathrm{~F}$ hf constants can thus be interpreted as resulting from unpaired electrons that are primarily located on the 3 d metal. Such a picture is also borne out in the values of the Mn hf constants. For $\mathrm{MnF}, \mathrm{b}_{\mathrm{F}}=413.65 \mathrm{MHz}-\mathrm{a}$ factor of 10 larger than that for the fluorine nucleus. In fact, on formation of $\mathrm{MnF}, 55 \%$ of the 4 s character is retained, in comparison with $\mathrm{Mn}^{+}$. $\left(\mathrm{A}_{\text {iso }}\left(\mathrm{Mn}^{+}\right)=770 \mathrm{MHz}\right.$ [24].) This result suggests that MnF is highly ionic, basically $\mathrm{Mn}^{+} \mathrm{F}^{-}$.

Large manganese Fermi contact parameters are found for many diatomic manganese species. As shown in Table $4, b_{F}$ falls in the range from 206.5 MHz for MnS [11] to 479.9 MHz in MnO [10]. The dipolar $c$ constant is correspondingly small. As the table also illustrates, $\mathrm{b}_{\mathrm{F}}$ decreases from MnO to $\mathrm{MnS}(479.9 \mathrm{MHz}$ to 206.5 MHz ), and from MnF to MnCl as well ( 413.6 MHz versus 376 MHz ). Such a trend suggests a decrease in ionicity as the columns of the periodic table are descended. Based on the $\mathrm{b}_{\mathrm{F}}$ values, MnH and MnS appear to be the most covalent of these compounds. One might expect MnF to be the most ionic, based
on electronegativity arguments. In contrast, the $\mathrm{b}_{\mathrm{F}}$ constants indicate that MnO has the highest degree of ionic character, a likely result of the contribution of the $\mathrm{Mn}^{2+} \mathrm{O}^{2-}$ structure.

## iii) Further Trends in 3d Metal Flourides

The 3d metal fluorides are thought to be predominantly ionic in character. Certainly MnH is less ionic than MnF , based on comparison of $\mathrm{b}_{\mathrm{F}}$ values. On the other hand, there may be a small increase in covalency across the 3d row. For example, Boldyrev and Simons suggest that titanium carries only +0.82 charge in TiF [25]. In contrast, Pouilly et al. [26] calculate that FeF is intermediate in its bonding character; $65 \%$ of the structure for iron fluoride is predicted to be ionic; the rest is thought to be covalent. No such calculations exist for MnF , so a direct comparison is difficult.

Some insight into the bonding in MnF can perhaps be gained by considering the trend in bond lengths. Of all 3 d transition metal fluorides, MnF has the longest bond distance, $\mathrm{r}_{0}=$ $1.839 \AA\left(\right.$ and $\mathrm{T}_{\mathrm{e}}=1.836 \AA$ ), with TiF having the second longest one ( $\left.\mathrm{r}_{0}=1.834[5]\right)$. CrF has a significantly shorter distance of $\mathrm{r}_{0}=1.788 \AA$, as does $\mathrm{FeF}(1.784 \AA)$ [27, 28]. Core contraction alone would suggest that the bond distances should steadily decrease across the 3 d row [1]. Clearly they do not.

Although the fluorides are chiefly ionic compounds, the abrupt increase in bond length at MnF can be understood in terms of a molecular orbital picture. The electron configuration in CrF is likely to be $9 \sigma^{1} 1 \delta^{2} 4 \pi^{2}$. Another electron is added to the orbitals in the formation of MnF , in this case the $10 \sigma$ antibonding orbital. This addition should increase the bond length, as it does. In FeF, the next electron adds to the 18 orbital, which is completely nonbonding and does little to influence the bond distance. Core contraction causes the bond length in FeF to shorten. An identical situation is observed in the 3d transition metal oxides [1, 21]. Another
comparison of note is the bond length in MnF relative to MnO . For the oxide, $\mathrm{r}_{0}=1.648 \mathrm{~A}$ [10], as opposed to $1.839 \AA$. The $0.2 \AA$ difference can be explained if MnO has partial $\mathrm{Mn}^{2+} \mathrm{O}^{2-}$ character ( MnF can only be $\mathrm{Mn}^{+} \mathrm{F}$ ); it also can be attributed to a higher bond order in MnO , as is found in TiO [29]. Hence, it is likely that some combination of ionic and covalent effects is influencing the behavior of these transition metal compounds.

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| $\mathrm{N}^{\prime}$ | j | $F_{i}$ | $\mathrm{F}^{\prime} \leftarrow$ | N | 1 | $F_{1}$ | F | $\mathrm{V}_{\text {cos }}$ | $\chi_{\text {absecalc }}$ | $\mathrm{N}^{\prime}$ | ${ }^{\prime}$ | $F_{1}$ | $F^{\prime} \leftarrow$ | N | 1 | $F_{1}$ | F | $V_{\text {obs }}$ | $V_{\text {obs }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 16 | 14 | 11.5 | 11 | 15 | 13 | 10.5 | 10 | 338373.656 | 0.573 | 16 | 19 | 19.5 | 19 | 15 | 18 | 18.5 | 18 | 338454.072 | 0.541 |
| 16 | 14 | 11.5 | 12 | 15 | 13 | 10.5 | 11 | 338373.656 | 0.097 | 16 | 18 | 18.5 | 19 | 15 | 17 | 17.5 | 18 | 338454.072 | -0.223 |
| 16 | 14 | 13.5 | 13 | is | 13 | 12.5 | 12 | 338373.656 | -0.296 | 16 | 19 | 19.5 | 20 | 15 | 18 | 18.5 | 19 | 338454.072 | -0.219 |
| 16 | 13 | 12.5 | 13 | 15 | 12 | 11.5 | 12 | 338375.506 | 0.320 | 16 | 18 | 19.5 | 20 | 15 | 17 | 18.5 | 19 | 338463.046 | -0.053 |
| 16 | 15 | 12.5 | 12 | 15 | 14 | 11.5 | 11 | 338377.526 | -0.141 | 16 | 18 | 19.5 | 19 | 15 | 17 | 18.5 | 18 | 338463.046 | 0.213 |
| 16 | 15 | 12.5 | $1 j$ | 15 | 14 | 11.5 | 12 | 338380.387 | <0.000 | 16 | 19 | 20.5 | 21 | 15 | 18 | 19.5 | 20 | 338468.192 | 0.209 |
| 16 | 14 | 12.5 | 13 | 15 | 13 | 11.5 | 12 | 338382.480 | -0.091 | 16 | 19 | 20.5 | 20 | 15 | 18 | 19.5 | 19 | 338468.192 | -0.265 |
| 16 | 13 | 13.5 | 13 | 15 | 12 | 12.5 | 12 | 338384.241 | -0.089 | 16 | 19 | 21.5 | 22 | 15 | 18 | 20.5 | 21 | 338469.814 | 0.141 |
| 16 | 14 | 13.5 | 14 | 15 | 13 | 12.5 | 13 | 338384.241 | -0.152 | 16 | 19 | 21.5 | 21 | 15 | 18 | 20.5 | 20 | 338469.814 | -0.191 |
| 16 | 16 | 13.5 | 13 | 15 | 15 | 12.5 | 12 | 338390.362 | -0.085 | 17 | 14 | 11.5 | 12 | 16 | 13 | 10.5 | 11 | 359484.332 | 0.083 |
| 16 | 15 | 13.5 | 14 | 15 | 14 | 12.5 | 13 | 338390.362 | -0.195 | 17 | 14 | 12.5 | 12 | 16 | 13 | 11.5 | 11 | 359484.332 | -0.139 |
| 16 | 16 | 13.5 | 14 | 15 | 15 | 12.5 | 13 | 338390.362 | -0.198 | 17 | 14 | 13.5 | 13 | 16 | 13 | 11.5 | 12 | 359488.448 | -0.276 |
| 16 | 15 | 13.5 | 13 | 15 | 14 | 12.5 | 12 | 338392.139 | -0.305 | 17 | 14 | 12.5 | 13 | 16 | 13 | 12.5 | 12 | 359488.448 | -0.573 |
| 16 | 16 | 14.5 | 14 | 15 | 15 | 13.5 | 13 | 338393.543 | -0.423 | 17 | 15 | 12.8 | 12 | 16 | 14 | 11.5 | 11 | 359493.677 | 0.339 |
| 16 | 15 | 15.5 | 16 | 15 | 15 | 14.5 | 15 | 338398.012 | 0.539 | 17 | is | 12/\$ | 13 | 16 | 14 | 11.5 | 12 | 359493.677 | -0.111 |
| 16 | 13 | 14.5 | 15 | 15 | 12 | 13.5 | 14 | 338398.012 | -0.240 | 17 | 15 | 14.5 | 14 | 16 | 14 | 13.5 | 13 | 359495.558 | -0.422 |
| 16 | 15 | 14.5 | 14 | 15 | 14 | 13.5 | 13 | 338398.012 | -0.520 | 17 | 14 | 13.5 | 14 | 16 | 13 | 12.5 | 13 | 359497.326 | 0.739 |
| 16 | 13 | 14.5 | 14 | 15 | 16 | 13.5 | 13 | 338399.826 | 0.257 | 17 | 15 | 13.5 | 14 | 16 | 14 | 12.5 | 13 | 359502.581 | -0.016 |
| 15 | 13 | 15.5 | 16 | 15 | 12 | 14.5 | 15 | 338399.826 | -0.246 | 17 | 15 | 13.5 | 13 | 16 | 14 | 12.5 | 12 | 359502.581 | -0.816 |
| 16 | 17 | 14.5 | 15 | 15 | 16 | 13.5 | 14 | 338401.797 | 0.091 | 17 | 15 | 14.5 | 15 | 16 | 14 | 13.5 | 14 | 359507.333 | 0.579 |
| 16 | 16 | 14.5 | 15 | 15 | 15 | 13.5 | 14 | 338401.797 | 0.012 | 17 | 15 | 15.5 | 15 | 16 | 14 | 14.5 | 14 | 359507.333 | 0.390 |
| 16 | 15 | 16.5 | 17 | 15 | 15 | 15.5 | 16 | 338407.381 | 0.047 | 17 | 16 | 14.5 | 15 | 16 | 15 | 13.5 | 14 | 359510.267 | -0.025 |
| 16 | 16 | 16.5 | 16 | 15 | 15 | 15.5 | 15 | 338407.381 | 0.011 | 17 | 14 | 14.5 | 15 | 16 | 13 | 13.5 | 14 | 359510.267 | 0.005 |
| 16 | 17 | 15.5 | 15 | 15 | 16 | 14.5 | 14 | 338407.381 | 0.032 | 17 | 17 | 14.5 | 14 | 16 | 16 | 13.5 | 13 | 359510.267 | -0.211 |
| 16 | 17 | 15.5 | 16 | 15 | 16 | 14.5 | 15 | 338416.014 | 0.317 | 17 | 17 | 14.5 | 15 | 16 | 16 | 13.5 | 14 | 359510.267 | -0.358 |
| 16 | 17 | 16.5 | 16 | 15 | 14 | 14.5 | 15 | 338416.014 | -0.348 | 17 | 16 | 14.5 | 14 | 16 | 15 | 13.5 | 13 | 359512.125 | 0.011 |
| 16 | 14 | 15.5 | 16 | 15 | 13 | 14.5 | 15 | 338416.014 | -0.580 | 17 | 16 | 15.5 | 16 | 16 | 15 | 14.5 | 15 | 359514.540 | <0.000 |
| 16 | 14 | 16.5 | 17 | 15 | 13 | 15.5 | 16 | 338418.732 | -0.247 | 17 | 17 | 15.5 | 15 | 16 | 16 | 14.5 | 14 | 359514.540 | -0.515 |
| 16 | 16 | 17.5 | 18 | 15 | 15 | 16.5 | 17 | 338420.007 | 0.497 | 17 | 16 | 15.5 | 15 | 16 | 15 | 14.5 | 14 | 359517.761 | -0.080 |
| 16 | 18 | 16.5 | 16 | 15 | 17 | 15.5 | 15 | 338420.007 | -0.450 | 17 | 14 | 15.5 | 16 | 16 | 13 | 14.5 | 15 | 359517.761 | -0.318 |
| 16 | 16 | 17.5 | 17 | 15 | 15 | 16.5 | 16 | 338421.488 | 0.360 | 17 | 16 | 16.5 | 16 | 16 | 15 | 15.5 | 15 | 359517.761 | -0.533 |
| 16 | 15 | 16.5 | 16 | 15 | 14 | 15.5 | 15 | 338423.136 | -0.578 | 17 | 14 | 15.5 | 15 | 16 | 13 | 14.5 | 14 | 359519.640 | 0.398 |
| 16 | 16 | 16.5 | 17 | 15 | 16 | 15.5 | 16 | 338427.754 | 0.049 | 17 | 17 | 16.5 | 16 | 16 | 16 | 15.5 | 15 | 359519.640 | 0.043 |
| 16 | 15 | 17.5 | 18 | 15 | 14 | 16.5 | 17 | 338429.914 | 0.257 | 17 | 18 | 15.5 | 15 | 16 | 17 | 14.5 | 14 | 359519.640 | 0.060 |
| 16 | 14 | 16.5 | 16 | 15 | 13 | 15.5 | 15 | 338429.914 | -0.118 | 17 | 14 | 16.5 | 17 | 16 | 13 | 15.5 | 16 | 359519.640 | -0.105 |
| 16 | 17 | 16.5 | 17 | 15 | 14 | 15.5 | 16 | 338429.914 | -0.298 | 17 | 18 | 15.5 | 16 | 16 | 17 | 14.5 | 15 | 359522.170 | 0.336 |
| 16 | 17 | 18.5 | 19 | 15 | 16 | 17.5 | 18 | 338432.518 | 0.421 | 17 | 17 | 15.5 | 16 | 16 | 16 | 14.5 | 15 | 359522.170 | -0.053 |
| 16 | 15 | 17.5 | 17 | 15 | 14 | 16.5 | 16 | 338432.518 | 0.321 | 17 | 16 | 17.5 | 18 | 16 | 15 | 16.5 | 17 | 359526.922 | 0.154 |
| 16 | 18 | 16.5 | 17 | 15 | 17 | 15.5 | 16 | 338434.575 | 0.081 | 17 | 16 | 17.5 | 17 | 16 | 16 | 16.5 | 16 | 359526.922 | 0.105 |
| 16 | 19 | 17.5 | 17 | 15 | 18 | 16.5 | 16 | 338436.982 | -0.528 | 17 | 18 | 16.5 | 16 | 16 | 17 | 15.5 | 15 | 359528.645 | 0.166 |
| 16 | 18 | 17.5 | 17 | 15 | 17 | 16.5 | 16 | 338438.512 | -0.087 | 17 | 19 | 16.5 | 16 | 16 | 18 | 15.5 | 15 | 359530.907 | -0.173 |
| 16 | 16 | 18.5 | 18 | 15 | 15 | 17.5 | 17 | 338439.803 | 0.274 | 17 | 19 | 16.5 | 17 | 16 | 18 | 15.5 | 16 | 359532.351 | 0.032 |
| 16 | 16 | 18.5 | 19 | 15 | 15 | 17.5 | 18 | 338441.894 | 0.685 | 17 | 15 | 16.5 | 16 | 16 | 14 | 15.5 | 15 | 359532.351 | -0.478 |
| 16 | 17 | 17.5 | 18 | 15 | 16 | 16.5 | 17 | 338441.894 | -0.052 | 17 | 17 | 16.5 | 17 | 16 | 16 | 15.5 | 16 | 359533.720 | 0.128 |
| 16 | 18 | 17.5 | 18 | 15 | 17 | 16.5 | 17 | 338441.894 | -0.343 | 17 | 18 | 16.5 | 17 | 16 | 17 | 15.5 | 16 | 359536.394 | 0.396 |
| 16 | 17 | 19.5 | 20 | 15 | 16 | 18.5 | 19 | 338445.119 | 0.285 | 17 | 15 | 16.5 | 17 | 16 | 14 | 15.5 | 16 | 359536.394 | -0.383 |
| 16 | 17 | 19.5 | 19 | 15 | 16 | 18.5 | 18 | 338445.119 | -0.298 | 17 | 17 | 17.5 | 17 | 16 | 17 | 16.5 | 16 | 359538.243 | 0.190 |
| 16 | 18 | 18.5 | 18 | 15 | 17 | 17.5 | 17 | 338451.884 | 0.131 | 17 | 19 | 17.5 | 18 | 16 | 14 | 16.5 | 17 | 359538.243 | -0.448 |


| $\mathrm{N}^{\mathrm{J}}$ | J' | $F_{i}^{\prime} \mathrm{F}$ | $\leftarrow$ | N | 1 | $F_{i}$ | F | $v_{\text {obs }}$ | $\nu_{\text {obscak }}$ | $\mathrm{N}^{\prime}$ | $\mathrm{J}^{\text {H }}$ | $\mathrm{F}_{i}$ | $F^{\prime}$ | N | 1 | $F_{1}$ | F | $\mathrm{V}_{\text {obs }}$ | olscalk. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 17 | 17 | 18.5 | 19 | 16 | 16 | 17.5 | 18 | 359539.686 | 0.476 | 18 | 17 | 16.5 | 16 | 17 | 16 | 15.5 | 15 | 380631.588 | 0.062 |
| 17 | 15 | 17.5 | 17 | 16 | 18 | 16.5 | 16 | 359539.686 | -0.424 | 18 | 17 | 17.5 | 17 | 17 | 16 | 16.5 | 16 | 380631.588 | -0.019 |
| 17 | 17 | 18.5 | 18 | 16 | 16 | 17.5 | 17 | 359541.237 | 0.497 | 18 | 15 | 17.5 | 18 | 17 | 14 | 16.5 | 17 | 380634.029 | 0.220 |
| 17 | 18 | 17.5 | 17 | 16 | 15 | 16.5 | 16 | 359544.462 | -0.060 | 18 | 19 | 16.5 | 16 | 17 | 18 | 15.5 | 15 | 380634.029 | -0.119 |
| 17 | 17 | 17.5 | 18 | 16 | 16 | 16.5 | 17 | 359547.914 | -0.036 | 18 | 19 | 16.5 | 17 | 17 | 18 | 15.5: | 16 | 380636.677 | 0.367 |
| 17 | 16 | 18.5 | 19 | 16 | 15 | 17.5 | 18 | 359550.079 | 0.398 | 18 | 18 | 16.5 | 17 | 17 | 17 | 15.5 | 16 | 380636.677 | -0.276 |
| 17 | 18 | 17.5 | 18 | 16 | 17 | 16.5 | 17 | 359550.079 | -0.296 | 18 | 17 | 18.5 | 19 | 17 | 16 | 17.5 | 18 | 380640.847 | 0.282 |
| 17 | 19 | 17.5 | 17 | 16 | 14 | 16.5 | 16 | 359550.079 | -0.483 | 18 | 19 | 18.5 | 18 | 17 | 16 | 17.5 | 17 | 380640.847 | 0.213 |
| 17 | 16 | 18.5 | 18 | 16 | 15 | 17.5 | 17 | 359552.212 | 0.152 | 18 | 19 | 17.5 | 17 | 17 | 18 | 16.5 | 16 | 380643.775 | -0.045 |
| 17 | 15 | 17.5 | 18 | 16 | 18 | 16.5 | 17 | 359554.795 | 0.010 | 18 | 18 | 17.5 | 18 | 17 | 17 | 16.5 | 17 | 380648.672 | 0.189 |
| 17 | 18 | 18.5 | 18 | 16 | 17 | 17.5 | 17 | 359556.061 | 0.019 | 18 | 19 | 17.5 | 18 | 17 | 18 | 16.5 | 17 | 380650.954 | 0.319 |
| 17 | 20 | 18.5 | 18 | 16 | 19 | 17.5 | 17 | 359557.662 | 0.014 | 18 | 16 | 17.5 | 18 | 17 | 15 | 16.5 | 17 | 380650.954 | -0.369 |
| 17 | 19 | 18.5 | 18 | 16 | 18 | 17.5 | 17 | 359559.121 | 0.312 | 18 | 18 | 19.5 | 20 | 17 | 17 | 18.5 | 19 | 380653.729 | 0.471 |
| 17 | 17 | 19.5 | 19 | 16 | 16 | 18.5 | 18 | 359559.121 | -0.475 | 18 | 18 | 18.5 | 18 | 17 | 17 | 17.5 | 17 | 380653.729 | -0.078 |
| 17 | 18 | 18.5 | 19 | 16 | 17 | 17.5 | 18 | 359561.731 | -0.094 | 18 | 16 | 18.5 | 18 | 17 | 15 | 17.5 | 17 | 380653.729 | -0.386 |
| 17 | 17 | 19.5 | 20 | 16 | 16 | 18.5 | 19 | 359561.731 | 0.520 | 18 | 18 | 19.5 | 19 | 17 | 17 | 18.5 | 18 | 380653.729 | -0.981 |
| 17 | 19 | 18.5 | 19 | 16 | 18 | 17.5 | 18 | 359561.731 | -0.430 | 18 | 17 | 18.5 | 18 | 17 | 18 | 17.5 | 17 | 380659.740 | 0.159 |
| 17 | 18 | 20.5 | 21 | 16 | 17 | 19.5 | 20 | 359564.975 | 0.348 | 18 | 18 | 18.5 | 19 | 17 | 17 | 17.5 | 18 | 380662.507 | -0.020 |
| 17 | 18 | 20.5 | 20 | 16 | 17 | 19.5 | 19 | 359564.975 | -0.195 | 18 | 17 | 19.5 | 20 | 17 | 16 | 18.5 | 19 | 380664.554 | 0.527 |
| 17 | 20 | 19.5 | 19 | 16 | 19 | 18.5 | 18 | 359567.795 | -0.103. | 18 | 19 | 18.5 | 19 | 17 | 18 | 17.5 | 18 | 380664.554 | -0.352 |
| 17 | 20 | 19.5 | 20 | 16 | 19 | 18.5 | 19 | 359569.375 | -0.090 | 18 | 19 | 20.5 | 20 | 17 | 18 | 19.5 | 19 | 380667.641 | 0.396 |
| 17 | 19 | 19.5 | 19 | 16 | 18 | 18.5 | 18 | 359571.526 | 0.049 | 18 | 21 | 18.5 | 19 | 17 | 20 | 17.5 | 18 | 380667.641 | 0.135 |
| 17 | 19 | 19.5 | 20 | 16 | 18 | 18.5 | 19 | 359573.748 | -0.026 | 18 | 16 | 18.5 | 19 | 17 | 15 | 17.5 | 18 | 380669.366 | -0.078 |
| 17 | 20 | 20.5 | 21 | 16 | 19 | 19.5 | 20 | 359573.748 | -0.264 | 18 | 20 | 19.5 | 19 | 17 | 19 | 18.5 | 18 | 380673.800 | 0.442 |
| 17 | 20 | 20.5 | 20 | 16 | 19 | 19.5 | 19 | 359573.748 | 0.499 | 18 | 18 | 20.5 | 20 | 17 | 17 | 19.5 | 19 | 380673.800 | -0.208 |
| 17 | 19 | 21.5 | 22 | 16 | 18 | 20.5 | 21 | 359577.322 | 0.129 | 18 | 19 | 19.5 | 20 | 17 | 18 | 18.5 | 19 | 380676.056 | -0.028 |
| 17 | 19 | 21.5 | 21 | 16 | 18 | 20.5 | 20 | 359577.322 | 0.210 | 18 | 18 | 20.5 | 21 | 17 | 17 | 19.5 | 20 | 380676.056 | 0.502 |
| 17 | 19 | 20.5 | 21 | 16 | 18 | 19.5 | 20 | 359582.273 | -0.064 | 18 | 20 | 19.5 | 20 | 17 | 19 | 18.5 | 19 | 380676.056 | -0.418 |
| 17 | 19 | 20.5 | 20 | 16 | 18 | 19.5 | 19 | 359582.273 | 0.268 | 18 | 19 | 21.5 | 22 | 17 | 18 | 20.5 | 21 | 380679.123 | 0.338 |
| 17 |  | 21.5 | 22 | 16 | 19 | 20.5 | 21 | 359587.540 | 0.256 | 18 | 19 | 21.5 | 21 | 17 | 18 | 20.5 | 20 | 380679.123 | -0.169 |
| 17 | 20 | 21.5 | 21 | 16 | 19 | 20.5 | 20 | 359587.540 | -0.102 | 18 | 21 | 20.5 | 20 | 17 | 20 | 19.5 | 19 | 380681.996 | -0.115 |
| 17 | 20 | 22.5 | 23 | 16 | 19 | 21.5 | 22 | 359589.543 | 0.227 | 18 | 21 | 20.5 | 21 | 17 | 20 | 19.5 | 20 | 380683.565 | -0.061 |
| 17 | 20 | 22.5 | 22 | 16 | 19 | 21.5 | 21 | 359589.543 | -0.054 | 18 | 20 | 20.5 | 20 | 17 | 19 | 19.5 | 19 | 380685.594 | 0.014 |
| 18 |  | 12.5 | 12 | 17 | 14 | 11.5 | 11 | 380597.403 | -0.176 | 18 | 20 | 20.5 | 21 | 17 | 19 | 19.5 | 20 | 380687.709 | 0.019 |
| 18 | 15 | 12.5 | 13 | 17 | 14 | 11.5 | 12 | 380599.372 | 0.332 | 18 | 21 | 21.5 | 22 | 17 | 20 | 20.5 | 21 | 380687.709 | -0.413 |
| 18 | 15 | 13.5 | 13 | 17 | 14 | 12.5 | 12 | 380599.372 | -0.309 | 18 | 21 | 21.5 | 21 | 17 | 20 | 20.5 | 20 | 380687.709 | 0.344 |
| 18 | 8 is | 14.5 | 14 | 17 | 14 | 13.5 | 13 | 380604.364 | -0.073 | 18 | 20 | 22.5 | 23 | 17 | 19 | 21.5 | 22 | 380691.423 | 0.125 |
| 18 | 8 is | IS 13.5 | 14 | 17 | 14 | 12.5 | 13 | 380604.364 | 0.087 | 18 | 20 | 22.5 | 22 | 17 | 19 | 21.5 | 21 | 380691.423 | 0.208 |
| 18 | 816 | 1613.5 | 13 | 17 | 15 | 12.5 | 12 | 380608.327 | 0.439 | 18 | 20 | 21.5 | 22 | 17 | 19 | 20.5 | 21 | 380695.920 | -0.132 |
| 18 | 816 | 1613.5 | 14 | 17 | 15 | 12.5 | 13 | 380608.327 | 0.020 | 18 | 20 | 21.5 | 21 | 17 | 19 | 20.5 | 20 | 380695.920 | 0.257 |
| 18 | 816 | 1615.5 | 15 | 17 | 14 | 13.5 | 14 | 380612.289 | 0.212 | 18 | 21 | 22.5 | 23 | 17 | 20 | 21.5 | 22 | 380701.247 | 0.196 |
| 18 | 815 | 1514.5 | 15 | 17 | 15 | 14.5 | 14 | 380612.289 | 0.215 | 18 | 21 | 22.5 | 22 | 17 | 20 | 21.5 | 21 | 380701.247 | -0.064 |
| 18 | 818 | 815.5 | 15 | 17 | 17 | 14.5 | 14 | 380624.962 | 0.113 | 18 | 21 | 23.5 | 24 | 17 | 20 | 22.5 | 23 | 380703.528 | 0.165 |
| 18 | 818 | 815.5 | 16 | 17 | 17 | 14.5 | 15 | 380624.962 | -0.060 | 18 | 21 | 23.5 | 23 | 17 | 20 | 22.5 | 22 | 380703.528 | -0.074 |
| 18 | 815 | 1515.5 | 16 | 17 | 14 | 14.5 | 15 | 380624.962 | -0.072 | 19 | 16 | 13.5 | 13 | 18 | 15 | 12.5 | 12 | 401706.138 | -0.117 |
| 18 | 817 | 716.5 | 17 | 17 | 16 | 15.5 | 16 | 380628.089 | -0.183 | 19 | 16 | 13.5 | 14 | 18 | 15 | 12.5 | 13 | 401708.306 | 0.549 |
| 18 | 817 | 717.5 | 18 | 17 | 16 | 16.5 | 17 | 380630.027 | 0.392 | 19 | 16 | 14.5 | 14 | 18 | 15 | 13.5 | 13 | 401708.306 | -0.495 |
| 18 | 818 | 816.5 | 16 | 17 | 17 | 15.5 | 15 | 380630.027 | -0.335 | 19 | 16 | 14.5 | 15 | 18 | 15 | 13.5 | 14 | 401713.761 | 0.375 |


| $\mathrm{N}^{\prime}$ | J | $F_{i}{ }^{\prime}$ | $\mathrm{F}^{\prime} \leftarrow$ | N | J | $F_{i}$ | F | $\nu_{\text {abs }}$ | $\nu_{\text {obsorak }}$ | $\mathrm{N}^{\prime}$ | j | $F_{1}$ | $\mathrm{F}^{\prime} \leftarrow$ | N | 1 | $F_{1}$ | F | $\nu_{\text {obs }}$ | $V_{\text {cos } \leq \text { al }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 19 | 16 | 15.5 | 15 | 18 | 15 | 14.5 | 14 | 401713.761 | -0.234 | 19 | 20 | 22.5 | 23 | 18 | 19 | 21.5 | 22 | 401787.228 | 0.255 |
| 19 | 17 | 14.5 | 14 | 18 | 16 | 13.5 | 13 | 401716.775 | 0.362 | 19 | 20 | 22.5 | 22 | 18 | 19 | 21.5 | 21 | 401787.228 | -0.221 |
| 19 | 17 | 14.5 | 15 | 18 | 16 | 13.5 | 14 | 401716.775 | -0.026 | 19 | 22 | 21.5 | 21 | 18 | 21 | 20.5 | 20 | 401790.289 | -0.090 |
| 19 | 17 | 16.5 | 16 | 18 | 16 | 15.5 | 15 | 401721.856 | 0.473 | 19 | 22 | 21.5 | 22 | 18 | 21 | 20.5 | 21 | 401791.809 | -0.032 |
| 19 | 16 | 15.5 | 16 | 18 | 15 | 14.5 | 15 | 401721.856 | -0.109 | 19 | 21 | 21.5 | 21 | 18 | 20 | 20.5 | 20 | 401793.727 | -0.007 |
| 19 | 17 | 15.5 | 16 | 18 | 16 | 14.5 | 15 | 401725.253 | -0.023 | 19 | 21 | 21.5 | 22 | 18 | 20 | 20.5 | 21 | 401795.878 | 0.181 |
| 19 | 17 | 15.5 | 15 | 18 | 16 | 14.5 | 14 | 401725.253 | -0.773 | 19 | 22 | 22.5 | 23 | 18 | 21 | 21.5 | 22 | 401795.878 | -0.404 |
| 19 | 16 | 16.5 | 16 | 18 | 15 | 15.5 | 15 | 401728.945 | -0.365 | 19 | 22 | 22.5 | 22 | 18 | 21 | 21.5 | 21 | 401795.878 | 0.340 |
| 19 | 17 | 16.5 | 17 | 18 | 16 | 15.5 | 16 | 401733.439 | 0.438 | 19 | 21 | 23.5 | 24 | 18 | 20 | 22.5 | 23 | 401799.546 | 0.094 |
| 19 | 19 | 16.5 | 16 | 18 | 18 | 15.5 | 15 | 401733.439 | 0.207 | 19 | 21 | 23.5 | 23 | 18 | 20 | 22.5 | 22 | 401799.546 | 0.178 |
| 19 | 19 | 16.5 | 17 | 18 | 18 | 15.5 | 16 | 401733.439 | 0.014 | 19 | 21 | 22.5 | 23 | 18 | 20 | 21.5 | 22 | 401803.717 | -0.171 |
| 19 | 16 | 16.5 | 17 | 18 | 15 | 15.5 | 16 | 401733.439 | -0.320 | 19 | 21 | 22.5 | 22 | 18 | 20 | 21.5 | 21 | 401803.717 | 0.264 |
| 19 | 18 | 16.5 | 16 | 18 | 17 | 15.5 | 15 | 401733.439 | -0.743 | 19 | 22 | 23.8 | 24 | 18 | 21 | 22.5 | 23 | 401809.115 | 0.187 |
| 19 | 18 | 17.5 | 18 | 18 | 17 | 16.5 | 17 | 401735.872 | -0.169 | 19 | 22 | 23.5 | 23 | 18 | 21 | 22.5 | 22 | 401809.115 | 0.008 |
| 19 | 17 | 18.5 | 19 | 18 | 17 | 17.5 | 18 | 401737.219 | 0.259 | 19 | 22 | 24.5 | 25 | 18 | 21 | 23.5 | 24 | 401811.513 | 0.040 |
| 19 | 18 | 18.5 | 18 | 18 | 17 | 17.5 | 17 | 401739.028 | 0.060 | 19 | 22 | 24.5 | 24 | 18 | 21 | 23.5 | 23 | 401811.513 | -0.162 |
| 19 | 18 | 17.5 | 17 | 18 | 17 | 16.5 | 16 | 401739.028 | -0.223 | 23 | 20 | 17.5 | 17 | 22 | 19 | 16.5 | 16 | 486074.110 | -0.003 |
| 19 | 19 | 17.5 | 17 | 18 | 18 | 16.5 | 16 | 401739.028 | -0.553 | 23 | 20 | 17.5 | 18 | 22 | 19 | 16.5 | 17 | 486076.108 | 0.540 |
| 19 | 16 | 17.5 | 17 | 18 | 15 | 16.5 | 16 | 401741.624 | 0.206 | 23 | 20 | 18.5 | 18 | 22 | 19 | 17.5 | 17 | 486078.166 | 0.047 |
| 19 | 16 | 18.5 | 19 | 18 | 15 | 17.5 | 18 | 401741.624 | -0.300 | 23 | 20 | 19.5 | 19 | 22 | 19 | 18.5 | 18 | 486084.661 | 0.024 |
| 19 | 20 | 17.5 | 18 | 18 | 19 | 16.5 | 17 | 401744.982 | 0.180 | 23 | 20 | 19.5 | 20 | 22 | 20 | 19.5 | 19 | 486090.920 | 0.050 |
| 19 | 19 | 17.5 | 18 | 18 | 18 | 16.5 | 17 | 401744.982 | -0.678 | 23 | 22 | 20.5 | 20 | 22 | 21 | 19.5 | 19 | 486100.372 | 0.438 |
| 19 | 17 | 17.5 | 18 | 18 | 16 | 16.5 | 17 | 401746.545 | -0.526 | 23 | 22 | 22.5 | 23 | 22 | 20 | 21.5 | 22 | 486100.372 | 0.227 |
| 19 | 18 | 19.5 | 20 | 18 | 17 | 18.5 | 19 | 401748.738 | 0.345 | 23 | 23 | 20.5 | 20 | 22 | 22 | 19.5 | 19 | 486100.372 | 0.093 |
| 19 | 20 | 19.5 | 19 | 18 | 19 | 18.5 | 18 | 401748.738 | 0.252 | 23 | 23 | 20.5 | 21 | 22 | 22 | 19.5 | 20 | 486100.372 | -0.140 |
| 19 | 20 | 18.5 | 18 | 18 | 19 | 17.5 | 17 | 401753.346 | 0.278 | 23 | 21 | 21.5 | 22 | 22 | 20 | 20.5 | 21 | 486100.372 | -0.453 |
| 19 | 21 | 18.5 | 18 | 18 | 20 | 17.5 | 17 | 401754.726 | 0.721 | 23 | 21 | 22.5 | 22 | 22 | 20 | 21.5 | 21 | 486102.759 | 0.532 |
| 19 | 18 | 18.5 | 19 | 18 | 20 | 17.5 | 18 | 401754.726 | -0.389 | 23 | 22 | 21.5 | 21 | 22 | 21 | 20.5 | 20 | 486104.103 | 0.246 |
| 19 | 19 | 18.5 | 19 | 18 | 18 | 17.5 | 18 | 401757.209 | -0.110 | 23 | 23 | 21.5 | 21 | 22 | 22 | 20.5 | 20 | 486104.103 | -0.971 |
| 19 | 20 | 18.5 | 19 | 18 | 19 | 17.5 | 18 | 401759.604 | 0.321 | 23 | 20 | 21.5 | 21 | 22 | 19 | 20.5 | 20 | 486108.101 | 0.459 |
| 19 | 21 | 18.5 | 19 | 18 | 16 | 17.5 | 18 | 401759.604 | -0.293 | 23 | 20 | 22.5 | 23 | 22 | 19 | 21.5 | 22 | 486108.101 | -0.060 |
| 19 | 19 | 20.5 | 21 | 18 | 18 | 19.5 | 20 | 401761.615 | 0.291 | 23 | 20 | 22.5 | 22 | 22 | 19 | 21.5 | 21 | 486108.101 | -0.584 |
| 19 | 21 | 19.5 | 19 | 18 | 16 | 18.5 | 18 | 401761.615 | -0.524 | 23 | 24 | 21.5 | 21 | 22 | 23 | 20.5 | 20 | 486110.836 | 0.270 |
| 19 | 19 | 19.5 | 19 | 18 | 18 | 18.5 | 18 | 401763.403 | 0.043 | 23 | 22 | 21.5 | 22 | 22 | 21 | 20.5 | 21 | 486113.310 | 0.281 |
| 19 | 18 | 19.5 | 19 | 18 | 17 | 18.5 | 18 | 401768.673 | 0.089 | 23 | 22 | 23.5 | 24 | 22 | 22 | 22.5 | 23 | 486113.310 | -0.077 |
| 19 | 20 | 21.5 | 22 | 18 | 19 | 20.5 | 21 | 401774.343 | 0.117 | 23 | 24 | 23.5 | 23 | 22 | 23 | 22.5 | 22 | 486113.310 | -0.278 |
| 19 | 17 | 19.5 | 19 | 18 | 20 | 18.5 | 18 | 401774.343 | 0.023 | 23 | 23 | 21.5 | 22 | 22 | 22 | 20.5 | 21 | 486113.310 | -0.499 |
| 19 | 18 | 20.5 | 20 | 18 | 17 | 19.5 | 19 | 401774.343 | -0.122 | 23 | 23 | 22.5 | 22 | 22 | 22 | 21.5 | 21 | 486119.042 | 0.262 |
| 19 | 22 | 19.5 | 20 | 18 | 21 | 18.5 | 19 | 401776.034 | 0.115 | 23 | 24 | 22.5 | 23 | 22 | 21 | 21.5 | 22 | 486122.242 | -0.034 |
| 19 | 17 | 19.5 | 20 | 18 | 16 | 18.5 | 19 | 401777.987 | -0.149 | 23 | 24 | 22.5 | 22 | 22 | 23 | 21.5 | 21 | 486122.242 | -0.625 |
| 19 | 20 | 20.5 | 20 | 18 | 19 | 19.5 | 19 | 401780.045 | 0.223 | 23 | 25 | 22.5 | 22 | 22 | 24 | 21.5 | 21 | 486125.208 | 0.151 |
| 19 | 22 | 20.5 | 20 | 18 | 21 | 19.5 | 19 | 401780.045 | -0.600 | 23 | 23 | 22.5 | 23 | 22 | 22 | 21.5 | 22 | 486125.208 | -0.609 |
| 19 | 21 | 20.5 | 20 | 18 | 20 | 19.5 | 19 | 401782.373 | 0.451 | 23 | 23 | 24.5 | 25 | 22 | 22 | 23.5 | 24 | 486127.727 | 0.565 |
| 19 | 19 | 21.5 | 21 | 18 | 18 | 20.5 | 20 | 401782.373 | -0.061 | 23 | 21 | 22.5 | 23 | 22 | 23 | 21.5 | 22 | 486127.727 | 0.335 |
| 19 | 20 | 20.5 | 21 | 18 | 19 | 19.5 | 20 | 401784.543 | 0.154 | 23 | 25 | 22.5 | 23 | 22 | 24 | 21.5 | 22 | 486127.727 | -0.060 |
| 19 | 19 | 21.5 | 22 | 18 | 18 | 20.5 | 21 | 401784.543 | 0.634 | 23 | 21 | 23.5 | 23 | 22 | 24 | 22.5 | 22 | 486127.727 | -0.109 |
| 19 | 21 | 20.5 | 21 | 18 | 20 | 19.5 | 20 | 401784.543 | -0.294 | 23 | 23 | 24.5 | 24 | 22 | 22 | 23.5 | 23 | 486127.727 | -0.596 |

Table 1 con'd.

| $\mathrm{N}^{\prime}$ | 1 | $F_{1}$ | $\mathrm{F}^{\prime} \leftarrow$ | N | J | $F_{1}$ | $F$ | $V_{\text {obs }}$ | $V_{\text {obs-calc }}$ | $\mathrm{N}^{\prime}$ | J | $F_{1}{ }^{\prime}$ | F' | 5 | N | J | $\mathrm{F}_{1}$ | F | $V_{\text {obs }}$ | $V_{\text {dos-rxic }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 23 | 23 | 23.5 | 23 | 22 | 22 | 22.5 | 22 | 486133.972 | 0.244 | 23 | 23 | 25.5 | 26 |  | 22 | 22 | 24.5 | 25 | 486151.662 | 0.825 |
| 23 | 25 | 23.5 | 23 | 22 | 21 | 22.5 | 22 | 486137.364 | -0.324 | 23 | 25 | 24.5 | 25 |  | 22 | 24 | 23.5 | 24 | 486151.662 | -0.400 |
| 23 | 23 | 23.5 | 24 | 22 | 23 | 22.5 | 23 | 486138.997 | 0.046 | 23 | 24 | 26.5 | 27 |  | 22 | 23 | 25.5 | 26 | 486153.699 | 0.329 |
| 23 | 22 | 24.5 | 25 | 22 | 21 | 23.5 | 24 | 486138.997 | -0.137 | 23 | 24 | 26.5 | 26 |  | 22 | 23 | 25.5 | 25 | 486153.699 | -0.039 |
| 23 | 22 | 24.5 | 24 | 22 | 21 | 23.5 | 23 | 486141.172 | 0.386 | 23 | 25 | 25.5 | 25 |  | 22 | 24 | 24.5 | 24 | 486160.083 | -0.133 |
| 23 | 25 | 23.5 | 24 | 22 | 24 | 22.5 | 23 | 486141.172 | -0.217 | 23 | 25 | 25.5 | 26 |  | 22 | 24 | 24.5 | 25 | 486162.287 | 0.473 |
| 23 | 24 | 25.5 | 25 | 22 | 23 | 24.5 | 24 | 486141.172 | -0.300 | 23 | 26 | 26.5 | 27 |  | 22 | 25 | 25.5 | 26 | 486162.287 | -0.418 |
| 23 | 21 | 23.5 | 24 | 22 | 25 | 22.5 | 23 | 486143.214 | 0.344 | 23 | 26 | 26.5 | 26 |  | 22 | 25 | 25.5 | 25 | 486162.287 | 0.247 |
| 23 | 22 | 23.5 | 23 | 22 | 20 | 22.5 | 22 | 486143.214 | -0.127 | 23 | 25 | 27.5 | 28 |  | 22 | 24 | 26.5 | 27 | 486165.869 | 0.054 |
| 23 | 26 | 23.5 | 23 | 22 | 25 | 22.5 | 22 | 486143.214 | -0.594 | 23 | 25 | 27.5 | 27 |  | 22 | 24 | 26.5 | 26 | 486165.869 | 0.120 |
| 23 | 26 | 23.5 | 24 | 22 | 21 | 22.5 | 23 | 486146.078 | -0.445 | 23 | 25 | 26.5 | 26 |  | 22 | 24 | 25.5 | 25 | 486169.135 | 0.192 |
| 23 | 24 | 24.5 | 24 | 22 | 23 | 23.5 | 23 | 485147.976 | -0.191 | 23 | 25 | 26.5 | 27 |  | 22 | 24 | 25.5 | 26 | 486169.135 | -0.362 |
| 23 | 26 | 24.5 | 24 | 22 | 25 | 23.5 | 23 | 486147.976 | -0.205 | 23 | 26 | 27.5 | 28 |  | 22 | 25 | 26.5 | 27 | 486174.550 | -0.067 |
| 23 | 23 | 25.5 | 25 | 22 | 22 | 24.5 | 24 | 486149.993 | 0.367 | 23 | 26 | 27.5 | 27 |  | 22 | 25 | 26.5 | 26 | 486174.550 | -0.031 |
| 23 | 25 | 24.5 | 24 | 22 | 24 | 23.5 | 23 | 486149.993 | 0.273 | 23 | 26 | 28.5 | 29 |  | 22 | 25 | 27.5 | 28 | 486177.634 | -0.127 |
| 23 | 26 | 24.5 | 25 | 22 | 25 | 23.5 | 24 | 486149.993 | -0.436 | 23 | 26 | 28.5 | 28 |  | 22 | 25 | 27.5 | 27 | 486177.634 | -0.229 |
| 23 | 24 | 24.5 | 25 | 22 | 23 | 23.5 | 24 | 486151.662 | 0.273 |  |  |  |  |  |  |  |  |  |  |  |

[^11]Table 2: Spectroscopic Parameters for $\mathrm{MnF}\left(\mathrm{X}^{7} \Sigma^{3}\right)^{\text {a) }}$

| Parameter | Millimeter-Wave |  | Optical | Matrix ESR |
| :---: | :---: | :---: | :---: | :---: |
|  | $y=0$ | $v=1$ | $\mathrm{v}=0$ |  |
| B | 10582.60503(47) | 10503.42888(38) | $10545(21)^{\text {b }}$ |  |
| D | 0.01383948(60) | $0.01383454(31)$ |  |  |
| $\gamma$ | $16.7152(30)$ | $16.3554(36)$ |  |  |
| $\hat{\lambda}$ | -136.511(96) | -142.3040(50) |  |  |
| $\lambda_{\text {D }}$ | $0.000927(40)$ | $0.0000195(50)$ |  |  |
| $\mathrm{b}_{\mathrm{F}}(\mathrm{Mn})$ | $413.615(30)$ | $434.277(30)$ |  |  |
| $\mathrm{c}(\mathrm{Mn})$ | 35.584(30) | $25.005(30)$ | 1 | $72(18)^{c}, 48(18)^{c}$ |
| $\mathrm{b}_{\mathrm{F}}(\mathrm{~F})$ | $\begin{gathered} 69.863(29) \\ 24^{\text {d }} \end{gathered}$ | $\begin{gathered} 72.40(19) \\ 24^{\mathrm{d}} \end{gathered}$ | 1 | $\begin{gathered} 68(6)^{\text {c) }}, 75(6)^{c} \\ \text { c) } \end{gathered}$ |
| mms | 0.204 | 0.244 |  |  |
| $\begin{aligned} & \mathrm{B}_{\mathrm{e}} \\ & \alpha_{\mathrm{e}} \end{aligned}$ | $\begin{gathered} 10622.19311(60) \\ 79.1762(12) \end{gathered}$ |  |  |  |

a) In MHz; errors are $3 \sigma$ and apply to the last quoted decimal places.
b) From ref [15]. Values originally quoted in $\mathrm{cm}^{-1}$.
c) From ref [14], neon matrix is first value, argon matrix is second value.
d) Held fixed (see text).

Table 3: ${ }^{19} \mathrm{~F}$ Hyperfine Parameters for Transition Metal Fluorides ${ }^{\text {a) }}$

| Molecule | $a$ | $b_{F}$ | $c$ | Configuration | Reference |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{TiF}\left(\mathrm{X}^{4} \Phi_{\mathrm{r}}\right)$ | $67.4(1.1)$ | $41(14)$ | $-28(14)$ | $9 \sigma^{1} 1 \delta^{1} 4 \pi^{1}$ | $[5]$ |
| $\mathrm{MnF}\left(\mathrm{X}^{7} \Sigma^{+}\right)$ | - | $69.863(29)$ | $24^{\mathrm{b}}$ | $9 \sigma^{1} 1 \delta^{2} 4 \pi^{2} 10 \sigma^{1}$ | This Work |
| $\mathrm{FeF}\left(\mathrm{X}^{6} \Delta_{i}\right)$ | $-0.45^{\mathrm{b})}$ | $91.7(3.7)$ | $51.7(3.5)$ | $9 \sigma^{1} 1 \delta^{3} 4 \pi^{2} 10 \sigma^{1}$ | $[28]$ |

a) In MHz ; errors are $3 \sigma$ and apply to the last quoted decimal places.
b) Held fixed (see text).

Table 4: Hyperfine Parameters for Manganese Diatomics ${ }^{\text {a) }}$

| Molecule | Ground State | $b_{f}$ | $c$ | Reference |
| :---: | :---: | :---: | :---: | :---: |
| MnH | ${ }^{7} \Sigma^{+}$ | $279(1)$ | $36.0(2.4)$ | $[8]$ |
| MnF | ${ }^{7} \Sigma^{+}$ | $413.615(30)$ | $35.584(30)$ | This Work |
| MnCl | ${ }^{7} \Sigma^{+}$ | $376(11)$ | $-102(30)$ | $[30]$ |
| MnO | ${ }^{6} \Sigma^{+}$ | $479.861(100)$ | $-48.199(178)$ | $[10]$ |
| MnS | ${ }^{6} \Sigma^{+}$ | $206.51(79)$ | $-27.8(1.6)$ | $[11]$ |

a) In MHz ; errors are $3 \sigma$ and apply to the last quoted decimal places.

## Figure Captions

Figure 1: Spectra of the $N=17 \leftarrow 16,19 \leftarrow 18$, and $23 \leftarrow 22$ rotational transitions of MnF $\left(\mathrm{X}^{7} \Sigma^{+}\right)$in its ground vibrational state near 359,401 , and 486 GHz , respectively. To a first approximation, each transition consists of 84 hyperfine components, arising from the electron spin and ${ }^{55} \mathrm{Mn}$ and ${ }^{19} \mathrm{~F}$ nuclear spins, condensed into a frequency range of about 100 MHz . These components are highly blended such that the fine/hyperfine pattern is not easily discernable in these data, although there are many repeating spectral features, which are traced by dashed lines across the spectra. Each spectrum is an average of four, one minute integrations over a 140 MHz frequency range.

Figure 2: The observed spectrum of the $\mathrm{N}=18 \leftarrow 17$ transition of $\mathrm{MnF}\left(\mathrm{X}^{7} \Sigma^{+}\right)$near 380 GHz (top panel) and a simulated spectrum of the same transition, based on the constants in Table 2 determined in the fit (lower panel). The simulated spectrum reproduces the features in the actual data quite well, verifying the accuracy of the analysis. The measured spectrum is 140 MHz wide in frequency, and is an average of four scans, each $\sim$ one minute in duration.


Frequency ( GHz )
Figure 1

$$
\operatorname{MnF}\left(X^{7} \Sigma^{+}: v=0\right) N=18 \longleftarrow 17
$$



Supplemental Table 1. Measured Rotational Transitions for $\mathrm{MnF}\left(\mathrm{X}^{7} \Sigma^{+}: v=1\right)^{\text {a) }}$

| $\mathrm{N}^{\mathbf{1}}$ | J | $F_{1}{ }^{\text {P }}$ | F | $\leftarrow$ | $\mathrm{N}^{n}$ | $\mathrm{J}^{\text {m }}$ | $\mathrm{F}_{1}{ }^{17}$ | $\mathrm{F}^{*}$ | $v_{\text {obs }}$ | $v_{\text {obs }}-v_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 18 | 18 | 16.5 | 16 |  | 17 | 17 | 15.5 | 15 | 377779.866 | 0.498 |
| 18 | 17 | 17.5 | 18 |  | 17 | 16 | 16.5 | 17 | 377779.866 | -0.554 |
| 18 | 15 | 16.5 | 16 |  | 17 | 14 | 15.5 | 15 | 377783.493 | -0.015 |
| 18 | 19 | 16.5 | 16 |  | 17 | 18 | 15.5 | 15 | 377783.493 | -0.262 |
| 18 | 19 | 16.5 | 17 |  | 17 | 18 | 15.5 | 16 | 377786.205 | -0.051 |
| 18 | 18 | 16.5 | 17 |  | 17 | 17 | 15.5 | 16 | 377786.205 | -0.508 |
| 18 | 17 | 18.5 | 19 |  | 17 | 16 | 17.5 | 18 | 377790.524 | -0.412 |
| 18 | 17 | 18.5 | 18 |  | 17 | 17 | 17.5 | 17 | 377790.524 | -0.477 |
| 18 | 19 | 17.5 | 17 |  | 17 | 18 | 16.5 | 16 | 377792.911 | 0.334 |
| 18 | 18 | 17.5 | 18 |  | 17 | 17 | 16.5 | 17 | 377797.681 | -0.192 |
| 18 | 19 | 17.5 | 18 |  | 17 | 18 | 16.5 | 17 | 377800.253 | 0.190 |
| 18 | 16 | 17.5 | 18 |  | 17 | 15 | 16.5 | 17 | 377800.253 | -0.563 |
| 18 | 18 | 18.5 | 19 |  | 17 | 17 | 17.5 | 18 | 377811.075 | -0.697 |
| 18 | 17 | 19.5 | 20 |  | 17 | 16 | 18.5 | 19 | 377813.750 | -0.141 |
| 18 | 20 | 18.5 | 18 |  | 17 | 15 | 17.5 | 17 | 377813.750 | -0.271 |
| 18 | 19 | 18.5 | 19 |  | 17 | 18 | 17.5 | 18 | 377813.750 | -0.265 |
| 18 | 17 | 19.5 | 19 |  | 17 | 16 | 18.5 | 18 | 377816.383 | 0.073 |
| 18 | 20 | 18.5 | 19 |  | 17 | 19 | 17.5 | 18 | 377818.608 | 0.381 |
| 18 | 18 | 20.5 | 21 |  | 17 | 17 | 19.5 | 20 | 377825.365 | 0.165 |
| 18 | 19 | 19.5 | 20 |  | 17 | 18 | 18.5 | 19 | 377825.365 | 0.094 |
| 18 | 20 | 19.5 | 20 |  | 17 | 19 | 18.5 | 19 | 377825.365 | -0.245 |
| 18 | 19 | 21.5 | 22 |  | 17 | 18 | 20.5 | 21 | 377828.388 | 0.169 |
| 18 | 19 | 21.5 | 21 |  | 17 | 18 | 20.5 | 20 | 377828.388 | -0.246 |
| 18 | 20 | 20.5 | 20 |  | 17 | 19 | 19.5 | 19 | 377834.321 | -0.485 |
| 18 | 20 | 20.5 | 21 |  | 17 | 19 | 19.5 | 20 | 377837.028 | 0.054 |
| 18 | 21 | 21.5 | 21 |  | 17 | 20 | 20.5 | 20 | 377837.028 | 0.186 |
| 18 | 21 | 21.5 | 22 |  | 17 | 20 | 20.5 | 21 | 377837.028 | -0.384 |
| 18 | 20 | 22.5 | 22 |  | 17 | 19 | 21.5 | 21 | 377840.625 | 0.057 |
| 18 | 20 | 22.5 | 23 |  | 17 | 19 | 21.5 | 22 | 377840.625 | 0.089 |
| 18 | 20 | 21.5 | 21 |  | 17 | 19 | 20.5 | 20 | 377845.325 | 0.204 |
| 18 | 20 | 21.5 | 22 |  | 17 | 19 | 20.5 | 21 | 377845.325 | -0.126 |
| 18 | 21 | 22.5 | 22 |  | 17 | 20 | 21.5 | 21 | 377850.490 | -0.241 |
| 18 | 21 | 22.5 | 23 |  | 17 | 20 | 21.5 | 22 | 377850.490 | 0.081 |
| 18 | 21 | 23.5 | 23 |  | 17 | 20 | 22.5 | 22 | 377852.686 | -0.022 |
| 18 | 21 | 23.5 | 24 |  | 17 | 20 | 22.5 | 23 | 377852.686 | 0.239 |
| 19 | 17 | 16.5 | 16 |  | 18 | 16 | 15.5 | 15 | 398712.891 | 0.288 |
| 19 | 16 | 15.5 | 16 |  | 18 | 15 | 14.5 | 15 | 398712.891 | -0.133 |
| 19 | 18 | 16.5 | 17 |  | 18 | 17 | 15.5 | 16 | 398724.467 | -0.193 |
| 19 | 19 | 16.5 | 16 |  | 18 | 18 | 15.5 | 15 | 398724.467 | -0.512 |
| 19 | 19 | 17.5 | 17 |  | 18 | 18 | 16.5 | 16 | 398730.518 | 0.213 |
| 19 | 16 | 17.5 | 18 |  | 18 | 15 | 16.5 | 17 | 398732.695 | 0.235 |
| 19 | 20 | 17.5 | 18 |  | 18 | 19 | 16.5 | 17 | 398736.754 | 0.341 |
| 19 | 19 | 18.5 | 19 |  | 18 | 18 | 17.5 | 18 | 398748.056 | -0.315 |
| 19 | 21 | 19.5 | 20 |  | 18 | 16 | 18.5 | 19 | 398752.724 | -0.273 |
| 19 | 19 | 20.5 | 21 |  | 18 | 18 | 19.5 | 20 | 398752.724 | -0.278 |
| 19 | 17 | 19.5 | 19 |  | 18 | 16 | 18.5 | 18 | 398754.293 | -0.054 |
| 19 | 19 | 20.5 | 20 |  | 18 | 18 | 19.5 | 19 | 398754.293 | -0.132 |
| 19 | 19 | 19.5 | 20 |  | 18 | 18 | 18.5 | 19 | 398762.201 | 0.209 |
| 19 | 20 | 21.5 | 22 |  | 18 | 19 | 20.5 | 21 | 398765.478 | -0.103 |
| 19 | 20 | 21.5 | 21 |  | 18 | 19 | 20.5 | 20 | 398766.852 | 0.108 |

Supplemental Table 1. Cont'd

| N | J | $\mathrm{F}_{1}{ }^{\text {a }}$ | F | $\leftarrow$ | $\mathrm{N}^{19}$ | $J^{\prime \prime}$ | $\mathrm{F}_{1}{ }^{\prime \prime}$ | $\mathrm{F}^{\text {w }}$ | $\nu_{\text {obs }}$ | $v_{\text {obs }}-V_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 19 | 22 | 19.5 | 20 |  | 18 | 21 | 18.5 | 19 | 398766.852 | -0.329 |
| 19 | 17 | 19.5 | 20 |  | 18 | 20 | 18.5 | 19 | 398768.852 | 0.299 |
| 19 | 17 | 19.5 | 20 |  | 18 | 20 | 18.5 | 19 | 398768.852 | 0.299 |
| 19 | 19 | 21.5 | 21 |  | 18 | 18 | 20.5 | 20 | 398773.289 | -0.472 |
| 19 | 19 | 21.5 | 22 |  | 18 | 18 | 20.5 | 21 | 398775.499 | 0.287 |
| 19 | 20 | 20.5 | 21 |  | 18 | 19 | 19.5 | 20 | 398775.499 | 0.294 |
| 19 | 21 | 20.5 | 21 |  | 18 | 20 | 19.5 | 20 | 398775.499 | -0.111 |
| 19 | 20 | 22.5 | 23 |  | 18 | 19 | 21.5 | 22 | 398778.127 | 0.058 |
| 19 | 20 | 22.5 | 22 |  | 18 | 19 | 21.5 | 21 | 398778.127 | -0.324 |
| 19 | 22 | 21.5 | 21 |  | 18 | 21 | 20.5 | 20 | 398781.343 | -0.027 |
| 19 | 22 | 21.5 | 22 |  | 18 | 21 | 20.5 | 21 | 398782.664 | -0.116 |
| 19 | 21 | 21.5 | 21 |  | 18 | 20 | 20.5 | 20 | 398784.763 | 0.175 |
| 19 | 21 | 21.5 | 22 |  | 18 | 20 | 20.5 | 21 | 398786.828 | 0.228 |
| 19 | 22 | 22.5 | 22 |  | 18 | 21 | 21.5 | 21 | 398786.828 | 0.183 |
| 19 | 22 | 22.5 | 23 |  | 18 | 21 | 21.5 | 22 | 398786.828 | -0.395 |
| 19 | 21 | 23.5 | 23 |  | 18 | 20 | 22.5 | 22 | 398790.396 | 0.031 |
| 19 | 21 | 23.5 | 24 |  | 18 | 20 | 22.5 | 23 | 398790.396 | 0.050 |
| 19 | 21 | 22.5 | 22 |  | 18 | 20 | 21.5 | 21 | 398794.770 | 0.257 |
| 19 | 21 | 22.5 | 23 |  | 18 | 20 | 21.5 | 22 | 398794.770 | -0.126 |
| 19 | 22 | 23.5 | 23 |  | 18 | 21 | 22.5 | 22 | 398799.749 | -0.392 |
| 19 | 22 | 23.5 | 24 |  | 18 | 21 | 22.5 | 23 | 398799.749 | -0.156 |
| 19 | 22 | 24.5 | 24 |  | 18 | 21 | 23.5 | 23 | 398802.363 | -0.071 |
| 19 | 22 | 24.5 | 25 |  | 18 | 21 | 23.5 | 24 | 398802.363 | 0.152 |
| 22 | 21 | 21.5 | 21 |  | 21 | 20 | 20.5 | 20 | 461539.390 | -0.228 |
| 22 | 19 | 20.5 | 21 |  | 21 | 18 | 19.5 | 20 | 461543.259 | 0.216 |
| 22 | 22 | 20.5 | 20 |  | 21 | 21 | 19.5 | 19 | 461543.259 | -0.158 |
| 22 | 19 | 20.5 | 20 |  | 21 | 18 | 19.5 | 19 | 461543.259 | -0.408 |
| 22 | 19 | 21.5 | 21 |  | 21 | 18 | 20.5 | 20 | 461545.474 | 0.370 |
| 22 | 23 | 20.5 | 20 |  | 21 | 22 | 19.5 | 19 | 461545.474 | -0.131 |
| 22 | 23 | 20.5 | 21 |  | 21 | 22 | 19.5 | 20 | 461547.511 | -0.171 |
| 22 | 22 | 20.5 | 21 |  | 21 | 21 | 19.5 | 20 | 461547.511 | -0.246 |
| 22 | 20 | 20.5 | 21 |  | 21 | 19 | 19.5 | 20 | 461549.395 | 0.558 |
| 22 | 22 | 22.5 | 23 |  | 21 | 22 | 21.5 | 22 | 461549.395 | -0.500 |
| 22 | 22 | 21.5 | 21 |  | 21 | 21 | 20.5 | 20 | 461552.609 | 0.618 |
| 22 | 23 | 21.5 | 21 |  | 21 | 22 | 20.5 | 20 | 461556.942 | 0.264 |
| 22 | 24 | 21.5 | 21 |  | 21 | 23 | 20.5 | 20 | 461556.942 | 0.183 |
| 22 | 20 | 21.5 | 21 |  | 21 | 19 | 20.5 | 20 | 461559.764 | 0.383 |
| 22 | 22 | 21.5 | 22 |  | 21 | 21 | 20.5 | 21 | 461559.764 | -0.618 |
| 22 | 23 | 21.5 | 22 |  | 21 | 22 | 20.5 | 21 | 461562.400 | 0.395 |
| 22 | 24 | 22.5 | 22 |  | 21 | 23 | 21.5 | 21 | 461564.529 | 0.241 |
| 22 | 22 | 23.5 | 23 |  | 21 | 21 | 22.5 | 22 | 461564.529 | 0.225 |
| 22 | 23 | 22.5 | 23 |  | 21 | 21 | 21.5 | 22 | 461573.881 | 0.451 |
| 22 | 24 | 22.5 | 23 |  | 21 | 23 | 21.5 | 22 | 461575.955 | 0.281 |
| 22 | 23 | 24.5 | 25 |  | 21 | 22 | 23.5 | 24 | 461575.955 | 0.026 |
| 22 | 25 | 22.5 | 23 |  | 21 | 24 | 21.5 | 22 | 461577.771 | -0.462 |
| 22 | 21 | 22.5 | 23 |  | 21 | 20 | 21.5 | 22 | 461580.588 | 0.185 |
| 22 | 23 | 23.5 | 23 |  | 21 | 22 | 22.5 | 22 | 461582.679 | 0.390 |
| 22 | 25 | 23.5 | 23 |  | 21 | 24 | 22.5 | 22 | 461582.679 | -0.243 |
| 22 | 24 | 23.5 | 23 |  | 21 | 23 | 22.5 | 22 | 461584.602 | 0.588 |
| 22 | 22 | 24.5 | 24 |  | 21 | 21 | 23.5 | 23 | 461584.602 | -0.170 |
| 22 | 25 | 23.5 | 24 |  | 21 | 24 | 22.5 | 23 | 461584.602 | -0.691 |

Supplemental Table 1. Cont'd

| N | J | $\mathrm{F}_{1}{ }^{\text {1 }}$ | $\mathrm{F}^{\text {a }}$ | $\leftarrow$ | $\mathrm{N}^{+1}$ | $\mathrm{J}^{\prime \prime}$ | $\mathrm{F}_{1}{ }^{\text {² }}$ | $\mathrm{F}^{69}$ | $v_{\text {obs }}$ | $\nu_{\text {obs }}-v_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 22 | 23 | 25.5 | 26 |  | 21 | 22 | 24.5 | 25 | 461588.586 | 0.094 |
| 22 | 23 | 25.5 | 25 |  | 21 | 22 | 24.5 | 24 | 461588.586 | -0.201 |
| 22 | 25 | 24.5 | 24 |  | 21 | 24 | 23.5 | 23 | 461592.461 | 0.410 |
| 22 | 25 | 24.5 | 25 |  | 21 | 24 | 23.5 | 24 | 461592.461 | -0.874 |
| 22 | 24 | 24.5 | 24 |  | 21 | 23 | 23.5 | 23 | 461595.046 | 0.100 |
| 22 | 24 | 24.5 | 25 |  | 21 | 23 | 23.5 | 24 | 461597.187 | 0.540 |
| 22 | 25 | 25.5 | 25 |  | 21 | 24 | 24.5 | 24 | 461597.187 | 0.132 |
| 22 | 25 | 25.5 | 26 |  | 21 | 24 | 24.5 | 25 | 461597.187 | -0.438 |
| 22 | 24 | 26.5 | 26 |  | 21 | 23 | 25.5 | 25 | 461600.735 | 0.012 |
| 22 | 24 | 26.5 | 27 |  | 21 | 23 | 25.5 | 26 | 461600.735 | 0.015 |
| 22 | 24 | 25.5 | 25 |  | 21 | 23 | 24.5 | 24 | 461604.352 | 0.314 |
| 22 | 24 | 25.5 | 26 |  | 21 | 23 | 24.5 | 25 | 461604.352 | -0.182 |
| 22 | 25 | 26.5 | 26 |  | 21 | 24 | 25.5 | 25 | 461609.676 | -0.015 |
| 22 | 25 | 26.5 | 27 |  | 21 | 24 | 25.5 | 26 | 461609.676 | 0.034 |
| 22 | 25 | 27.5 | 27 |  | 21 | 24 | 26.5 | 26 | 461612.448 | -0.208 |
| 22 | 25 | 27.5 | 28 |  | 21 | 24 | 26.5 | 27 | 461612.448 | -0.069 |
| 23 | 20 | 20.5 | 20 |  | 22 | 19 | 19.5 | 19 | 482456.176 | -0.151 |
| 23 | 23 | 20.5 | 20 |  | 22 | 22 | 19.5 | 19 | 482458.874 | 0.056 |
| 23 | 22 | 20.5 | 20 |  | 22 | 21 | 19.5 | 19 | 482458.874 | -0.050 |
| 23 | 23 | 20.5 | 21 |  | 22 | 22 | 19.5 | 20 | 482458.874 | -0.315 |
| 23 | 21 | 22.5 | 22 |  | 22 | 21 | 21.5 | 21 | 482462.129 | 0.564 |
| 23 | 21 | 20.5 | 21 |  | 22 | 20 | 19.5 | 20 | 482462.129 | -0.123 |
| 23 | 20 | 21.5 | 22 |  | 22 | 19 | 20.5 | 21 | 482465.783 | 0.039 |
| 23 | 20 | 21.5 | 21 |  | 22 | 19 | 20.5 | 20 | 482465.783 | -0.530 |
| 23 | 20 | 22.5 | 22 |  | 22 | 19 | 21.5 | 21 | 482468.341 | 0.632 |
| 23 | 24 | 21.5 | 21 |  | 22 | 23 | 20.5 | 20 | 482468.341 | -0.273 |
| 23 | 23 | 21.5 | 22 |  | 22 | 20 | 20.5 | 21 | 482471.815 | -0.067 |
| 23 | 23 | 23.5 | 24 |  | 22 | 22 | 22.5 | 23 | 482471.815 | -0.415 |
| 23 | 24 | 23.5 | 23 |  | 22 | 23 | 22.5 | 22 | 482471.815 | -0.609 |
| 23 | 23 | 22.5 | 22 |  | 22 | 22 | 21.5 | 21 | 482476.429 | 0.634 |
| 23 | 25 | 22.5 | 22 |  | 22 | 20 | 21.5 | 21 | 482482.951 | 0.390 |
| 23 | 23 | 22.5 | 23 |  | 22 | 22 | 21.5 | 22 | 482482.951 | -0.540 |
| 23 | 24 | 22.5 | 23 |  | 22 | 23 | 21.5 | 22 | 482485.356 | 0.309 |
| 23 | 23 | 24.5 | 25 |  | 22 | 22 | 23.5 | 24 | 482485.356 | -0.221 |
| 23 | 25 | 22.5 | 23 |  | 22 | 24 | 21.5 | 22 | 482485.356 | -0.196 |
| 23 | 21 | 23.5 | 24 |  | 22 | 20 | 22.5 | 23 | 482485.356 | -0.227 |
| 23 | 22 | 23.5 | 23 |  | 22 | 21 | 22.5 | 22 | 482494.971 | 0.216 |
| 23 | 24 | 23.5 | 24 |  | 22 | 23 | 22.5 | 23 | 482496.562 | 0.159 |
| 23 | 24 | 25.5 | 26 |  | 22 | 23 | 24.5 | 25 | 482498.909 | 0.363 |
| 23 | 25 | 23.5 | 24 |  | 22 | 24 | 22.5 | 23 | 482498.909 | 0.229 |
| 23 | 22 | 24.5 | 24 |  | 22 | 21 | 23.5 | 23 | 482498.909 | -0.303 |
| 23 | 24 | 25.5 | 25 |  | 22 | 23 | 24.5 | 24 | 482498.909 | -0.644 |
| 23 | 21 | 23.5 | 23 |  | 22 | 20 | 22.5 | 22 | 482500.748 | 0.563 |
| 23 | 26 | 23.5 | 24 |  | 22 | 25 | 22.5 | 23 | 482500.748 | -0.287 |
| 23 | 22 | 23.5 | 24 |  | 22 | 21 | 22.5 | 23 | 482503.218 | -0.311 |
| 23 | 24 | 24.5 | 25 |  | 22 | 23 | 23.5 | 24 | 482509.145 | 0.383 |
| 23 | 24 | 24.5 | 25 |  | 22 | 23 | 23.5 | 24 | 482509.145 | 0.383 |
| 23 | 25 | 24.5 | 25 |  | 22 | 24 | 23.5 | 24 | 482509.145 | -0.279 |
| 23 | 24 | 26.5 | 27 |  | 22 | 23 | 25.5 | 26 | 482511.320 | 0.174 |
| 23 | 24 | 26.5 | 26 |  | 22 | 23 | 25.5 | 25 | 482511.320 | -0.096 |
| 23 | 26 | 25.5 | 25 |  | 22 | 25 | 24.5 | 24 | 482515.419 | 0.601 |

Supplemental Table 1. Cont'd

| N | J | $\mathrm{F}_{1}{ }^{\text {a }}$ | F' | $\leftarrow$ | $\mathrm{N}^{\text {m }}$ | $\mathrm{J}^{\prime \prime}$ | $\mathrm{F}_{1}{ }^{\text {² }}$ | $\mathrm{F}^{\text {w }}$ | $\nu_{\text {obs }}$ | $\nu_{\text {obs }}-\nu_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 23 | 26 | 25.5 | 26 |  | 22 | 25 | 24.5 | 25 | 482515.419 | -0.643 |
| 23 | 25 | 25.5 | 26 |  | 22 | 24 | 24.5 | 25 | 482519.861 | 0.608 |
| 23 | 26 | 26.5 | 26 |  | 22 | 25 | 25.5 | 25 | 482519.861 | 0.126 |
| 23 | 26 | 26.5 | 27 |  | 22 | 25 | 25.5 | 26 | 482519.861 | -0.434 |
| 23 | 25 | 27.5 | 27 |  | 22 | 24 | 26.5 | 26 | 482523.398 | 0.020 |
| 23 | 25 | 27.5 | 28 |  | 22 | 24 | 26.5 | 27 | 482523.398 | 0.022 |
| 23 | 25 | 26.5 | 26 |  | 22 | 24 | 25.5 | 25 | 482526.811 | 0.301 |
| 23 | 25 | 26.5 | 27 |  | 22 | 24 | 25.5 | 26 | 482526.811 | -0.221 |
| 23 | 26 | 27.5 | 27 |  | 22 | 25 | 26.5 | 26 | 482532.196 | 0.034 |
| 23 | 26 | 27.5 | 28 |  | 22 | 25 | 26.5 | 27 | 482532.196 | 0.038 |
| 23 | 26 | 28.5 | 28 |  | 22 | 25 | 27.5 | 27 | 482535.145 | -0.140 |
| 23 | 26 | 28.5 | 29 |  | 22 | 25 | 27.5 | 28 | 482535.145 | -0.022 |
| 24 | 21 | 18.5 | 18 |  | 23 | 20 | 17.5 | 17 | 503348.864 | 0.160 |
| 24 | 21 | 19.5 | 20 |  | 23 | 20 | 18.5 | 19 | 503356.749 | -0.056 |
| 24 | 22 | 20.5 | 20 |  | 23 | 21 | 19.5 | 19 | 503366.984 | 0.249 |
| 24 | 21 | 20.5 | 21 |  | 23 | 20 | 19.5 | 20 | 503366.984 | -0.195 |
| 24 | 23 | 21.5 | 21 |  | 23 | 22 | 20.5 | 20 | 503373.715 | -0.092 |
| 24 | 23 | 23.5 | 24 |  | 23 | 21 | 22.5 | 23 | 503373.715 | -0.145 |
| 24 | 21 | 21.5 | 22 |  | 23 | 20 | 20.5 | 21 | 503376.046 | 0.385 |
| 24 | 22 | 23.5 | 23 |  | 23 | 21 | 22.5 | 22 | 503376.046 | 0.149 |
| 24 | 23 | 22.5 | 22 |  | 23 | 22 | 21.5 | 21 | 503378.221 | 0.573 |
| 24 | 24 | 22.5 | 22 |  | 23 | 21 | 20.5 | 21 | 503378.221 | -0.190 |
| 24 | 21 | 22.5 | 23 |  | 23 | 20 | 21.5 | 22 | 503380.644 | -0.166 |
| 24 | 23 | 22.5 | 23 |  | 23 | 22 | 21.5 | 22 | 503386.754 | 0.223 |
| 24 | 23 | 24.5 | 25 |  | 23 | 23 | 23.5 | 24 | 503386.754 | -0.184 |
| 24 | 25 | 24.5 | 24 |  | 23 | 24 | 23.5 | 23 | 503386.754 | -0.405 |
| 24 | 24 | 22.5 | 23 |  | 23 | 23 | 21.5 | 22 | 503386.754 | -0.525 |
| 24 | 24 | 23.5 | 23 |  | 23 | 23 | 22.5 | 22 | 503392.427 | 0.566 |
| 24 | 23 | 23.5 | 23 |  | 23 | 22 | 22.5 | 22 | 503394.708 | -0.239 |
| 24 | 25 | 23.5 | 23 |  | 23 | 24 | 22.5 | 22 | 503396.381 | 0.544 |
| 24 | 25 | 23.5 | 24 |  | 23 | 22 | 22.5 | 23 | 503396.381 | 0.515 |
| 24 | 24 | 25.5 | 26 |  | 23 | 23 | 24.5 | 25 | 503400.614 | 0.151 |
| 24 | 25 | 24.5 | 25 |  | 23 | 21 | 23.5 | 24 | 503400.614 | 0.141 |
| 24 | 22 | 23.5 | 24 |  | 23 | 24 | 22.5 | 23 | 503400.614 | 0.163 |
| 24 | 24 | 24.5 | 25 |  | 23 | 24 | 23.5 | 24 | 503411.521 | -0.218 |
| 24 | 26 | 24.5 | 25 |  | 23 | 25 | 23.5 | 24 | 503414.074 | 0.018 |
| 24 | 23 | 25.5 | 25 |  | 23 | 22 | 24.5 | 24 | 503414.074 | -0.120 |
| 24 | 23 | 24.5 | 24 |  | 23 | 21 | 23.5 | 23 | 503416.355 | 0.545 |
| 24 | 22 | 24.5 | 25 |  | 23 | 26 | 23.5 | 24 | 503416.355 | 0.177 |
| 24 | 27 | 24.5 | 25 |  | 23 | 22 | 23.5 | 24 | 503419.037 | 0.016 |
| 24 | 26 | 25.5 | 25 |  | 23 | 25 | 24.5 | 24 | 503422.521 | 0.186 |
| 24 | 24 | 26.5 | 26 |  | 23 | 23 | 25.5 | 25 | 503422.521 | -0.259 |
| 24 | 25 | 27.5 | 28 |  | 23 | 24 | 26.5 | 27 | 503426.364 | 0.195 |
| 24 | 25 | 27.5 | 27 |  | 23 | 24 | 26.5 | 26 | 503426.364 | -0.050 |
| 24 | 27 | 26.5 | 26 |  | 23 | 26 | 25.5 | 25 | 503430.650 | 0.687 |
| 24 | 27 | 26.5 | 27 |  | 23 | 26 | 25.5 | 26 | 503430.650 | -0.517 |
| 24 | 26 | 26.5 | 27 |  | 23 | 25 | 25.5 | 26 | 503434.837 | 0.580 |
| 24 | 27 | 27.5 | 27 |  | 23 | 26 | 26.5 | 26 | 503434.837 | 0.042 |
| 24 | 27 | 27.5 | 28 |  | 23 | 26 | 26.5 | 27 | 503434.837 | -0.507 |
| 24 | 26 | 28.5 | 29 |  | 23 | 25 | 27.5 | 28 | 503438.393 | -0.015 |
| 24 | 26 | 28.5 | 28 |  | 23 | 25 | 27.5 | 27 | 503438.393 | -0.015 |

Supplemental Table 1. Cont'd

| $\mathrm{N}^{\text {s }}$ | J | $\mathrm{F}_{1}{ }^{\text {1 }}$ | F ${ }^{\text {d }}$ | $\leftarrow$ | $\mathrm{N}^{3 /}$ | $\mathrm{J}^{\prime \prime}$ | $\mathrm{F}_{1}{ }^{\text {m }}$ | $\mathrm{F}^{\text {m }}$ | $V_{\text {obs }}$ | $v_{\text {obs }}-v_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 24 | 26 | 27.5 | 27 |  | 23 | 25 | 26.5 | 26 | 503441.553 | 0.158 |
| 24 | 26 | 27.5 | 28 |  | 23 | 25 | 26.5 | 27 | 503441.553 | -0.385 |
| 30 | 27 | 27.5 | 27 |  | 29 | 26 | 26.5 | 26 | 628685.869 | -0.093 |
| 30 | 30 | 27.5 | 27 |  | 29 | 29 | 26.5 | 26 | 628685.869 | -0.215 |
| 30 | 29 | 30.5 | 31 |  | 29 | 28 | 29.5 | 30 | 628696.333 | -0.123 |
| 30 | 30 | 30.5 | 30 |  | 29 | 28 | 29.5 | 29 | 628696.333 | -0.470 |
| 30 | 31 | 28.5 | 28 |  | 29 | 30 | 27.5 | 27 | 628696.333 | -0.752 |
| 30 | 29 | 28.5 | 29 |  | 29 | 28 | 27.5 | 28 | 628701.209 | 0.882 |
| 30 | 30 | 28.5 | 29 |  | 29 | 29 | 27.5 | 28 | 628701.209 | 0.654 |
| 30 | 29 | 29.5 | 29 |  | 29 | 30 | 28.5 | 28 | 628707.420 | 0.027 |
| 30 | 30 | 29.5 | 29 |  | 29 | 29 | 28.5 | 28 | 628707.420 | -0.439 |
| 30 | 29 | 29.5 | 30 |  | 29 | 28 | 28.5 | 29 | 628707.420 | -0.477 |
| 30 | 31 | 29.5 | 29 |  | 29 | 28 | 28.5 | 28 | 628711.059 | 0.423 |
| 30 | 30 | 31.5 | 32 |  | 29 | 29 | 30.5 | 31 | 628711.059 | 0.173 |
| 30 | 28 | 30.5 | 31 |  | 29 | 27 | 29.5 | 39 | 628711.059 | 0.124 |
| 30 | 31 | 29.5 | 30 |  | 29 | 30 | 28.5 | 29 | 628713.968 | 0.079 |
| 30 | 32 | 29.5 | 30 |  | 29 | 31 | 28.5 | 29 | 628713.968 | -0.151 |
| 30 | 32 | 30.5 | 31 |  | 29 | 31 | 29.5 | 30 | 628727.665 | 0.189 |
| 30 | 30 | 30.5 | 31 |  | 29 | 29 | 29.5 | 30 | 628727.665 | 0.015 |
| 30 | 33 | 30.5 | 30 |  | 29 | 32 | 29.5 | 29 | 628730.725 | 0.296 |
| 30 | 30 | 32.5 | 32 |  | 29 | 29 | 31.5 | 31 | 628734.708 | -0.104 |
| 30 | 33 | 31.5 | 32 |  | 29 | 32 | 30.5 | 31 | 628734.708 | -0.452 |
| 30 | 32 | 31.5 | 31 |  | 29 | 31 | 30.5 | 30 | 628734.708 | -0.727 |
| 30 | 32 | 31.5 | 32 |  | 29 | 31 | 30.5 | 31 | 628737.203 | -0.070 |
| 30 | 31 | 33.5 | 34 |  | 29 | 30 | 32.5 | 33 | 628737.203 | -0.224 |
| 30 | 31 | 33.5 | 33 |  | 29 | 30 | 32.5 | 32 | 628737.203 | -0.329 |
| 30 | 33 | 32.5 | 32 |  | 29 | 32 | 31.5 | 31 | 628742.517 | 0.457 |
| 30 | 33 | 32.5 | 33 |  | 29 | 32 | 31.5 | 32 | 628742.517 | -0.536 |
| 30 | 32 | 32.5 | 33 |  | 29 | 31 | 31.5 | 32 | 628746.549 | 0.712 |
| 30 | 33 | 33.5 | 33 |  | 29 | 32 | 32.5 | 32 | 628746.549 | 0.142 |
| 30 | 33 | 33.5 | 34 |  | 29 | 32 | 32.5 | 33 | 628746.549 | -0.319 |
| 30 | 32 | 34.5 | 34 |  | 29 | 31 | 33.5 | 33 | 628749.580 | -0.231 |
| 30 | 32 | 34.5 | 35 |  | 29 | 31 | 33.5 | 34 | 628749.580 | -0.220 |
| 30 | 32 | 33.5 | 33 |  | 29 | 31 | 32.5 | 32 | 628752.673 | 0.235 |
| 30 | 32 | 33.5 | 34 |  | 29 | 31 | 32.5 | 33 | 628752.673 | -0.369 |
| 30 | 33 | 34.5 | 34 |  | 29 | 32 | 33.5 | 33 | 628758.033 | 0.051 |
| 30 | 33 | 34.5 | 35 |  | 29 | 32 | 33.5 | 34 | 628758.033 | -0.121 |
| 30 | 33 | 35.5 | 35 |  | 29 | 32 | 34.5 | 34 | 628761.281 | -0.416 |
| 30 | 33 | 35.5 | 36 |  | 29 | 32 | 34.5 | 35 | 628761.281 | -0.386 |

a) $\operatorname{In} \mathrm{MHz}$.

## APPENDIX K

LABORATORY DETECTION OF THE COCN $\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ RADICAL.
P. M. Sheridan and L. M. Zurys, J. Chem. Phys., in preparation (DRAFT).

# Laboratory Detection of the $\operatorname{CoCN} \operatorname{Radical}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ 

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#### Abstract

The millimeter/sub-millimeter wave spectrum of the CoCN radical has been recorded in the frequency range $350-500 \mathrm{GHz}$ using direct absorption techniques. This study is the first spectroscopic observation of this molecule in the laboratory. The ground state has been assigned as ${ }^{3} \Phi_{1}$ based on the observation of three ground state spin-orbit components and in analogy with $\operatorname{CoH}\left(X^{3} \Phi_{i}\right), \operatorname{CoF}\left(X^{3} \Phi_{i}\right)$, and $\operatorname{CoCl}\left(X^{3} \Phi_{i}\right)$. Rotational transitions arising from the $\Omega=4,3$, and 2 spin-orbit components have been recorded, with hyperfine splittings arising from the ${ }^{59} \mathrm{Co}(\mathrm{I}=7 / 2)$ nucleus resolved in each. For the main isotope, several additional rotational transitions were observed within the lowest bending vibrational components, which exhibited Renner-Teller splittings, and in the first quantum of the metal-carbon stretch. The ground state data were fit using a case ( $a_{\beta}$ ) Hamiltonian and the vibronic components were modeled using an effective expression that contains the diagonal portion of the magnetic hyperfine Hamiltonian. In addition, transitions arising from the $\mathrm{Co}^{13} \mathrm{CN}$ isotopomer were recorded as well. Based on the isotopic data, an $r_{0}$ structure was calculated, and this radical was found to have a linear cyanide geometry, similar to the $\mathrm{ZnCN}, \mathrm{CuCN}$, and NiCN . The linear cyanide structure suggests that the bonding in CoCN is largely covalent, like nickel, copper, and zinc cyanides. The hyperfine parameters determined for CoCN are similar to those measured for CoH and CoCl ; the latter suggests that CoCN has a greater ionic bonding character than these other cyanides.


## 1. Introduction

Three distinct structures have been observed for metal cyanides. Sodium and potassium exhibit a $t$-shaped geometry in which the metal orbits the cyanide moiety in a highly ionic, polytopic bond.[1,2] Lithium, the alkaline-earth, and the group-13 metals[3-6] are found to possess the linear isocyanide structure due to an increase in the covalent bonding character.[7,8] Prior to recent investigations of the transition metal cyanides, the linear cyanide geometry had only been encountered as a higher energy isomer.[9]

The first transition metal cyanide to be observed was FeNC.[10] This species was found to have the linear isocyanide form, like the previously observed metal cyanides. This work was followed by millimeter-wave studies investigations of $\mathrm{ZnCN}\left(\mathrm{X}^{2} \Sigma^{5}\right)$ and $\mathrm{CuCN}\left(\mathrm{X}^{1} \Sigma^{+}\right)$. These measurements unambiguously determined that they both possessed the linear cyanide structure.[11,12] Laser induced fluorescence studies of $\mathrm{NiCN}\left(\mathrm{X}^{2} \Delta_{i}\right)$ showed that this radical also exhibited the linear cyanide form,[13] with measurement of the pure rotational spectrum confirming this geometry.[14] Unfortunately, the remaining transition metal cyanides have received almost no attention, both theoretically and experimentally; therefore, their ground state geometric forms are not known. Cobalt cyanide occupies a very curious position between NiCN , a cyanide, and FeNC , an isocyanide, making its structure of particular interest.

Spectroscopic investigations of cobalt containing radicals, in general, have been limited. For example, only the pure rotational spectrum of $\operatorname{CoC}\left(\mathrm{X}^{2} \Sigma^{+}\right)$has been measured to completion.[15] Pure rotational transitions of $\mathrm{CoO}\left(\mathrm{X}^{4} \Delta_{i}\right)$ have also been recorded[16]; however, only in the lowest two spin-orbit components prohibiting a
complete case(a) analysis. Laser magnetic resonance (LMR) spectroscopic studies of $\mathrm{CoH}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ have only identified the two lowest spin-orbit components of this molecule [17] and pure rotational transitions of $\operatorname{CoF}\left(\mathrm{X}^{3} \Phi_{i}\right)$ have been recently recorded only in the $\Omega=4$ ground state spin sub-level[18]. In all three cases large hyperfine splittings due to ${ }^{59} \mathrm{Co}(\mathrm{I}=7 / 2)$ were observed. Electronic transitions of $\mathrm{CoH}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right), \mathrm{CoF}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$, and $\operatorname{CoCl}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ have also been measured; [19-22] however, only for CoF have all three spinorbit components been identified. A large spin-orbit energy separation exists in these molecules, making observation of all spin-components difficult, especially under jetcooled conditions. For CoCl , cobalt hyperfine splittings have also been measured.

In this paper, we report the first detection of the CoCN radical. The ground state has been assigned as $X^{3} \Phi_{i}$, based on the observation of three ground state spin-orbit components and in analogy with $\mathrm{CoH}, \mathrm{CoF}$, and CoCl . Rotational transitions arising from the $\Omega=4,3$, and 2 spin-orbit sub-levels, as well as several vibronic states, were recorded. In order to determine the geometry of the molecule, rotational transitions of the $\mathrm{Co}^{13} \mathrm{CN}$ isotopomer were also measured. An analysis of the spectroscopic data and a discussion of the structure and bonding properties of CoCN and other cyanides follow.

## II. Experimental

Pure rotational transitions of CoCN were recorded using the high temperature millimeter-wave spectrometer of the Ziurys group.[23] Briefly, the instrument consists of a set phase-locked Gunn oscillators and Schottky-diode multiplier ( $65-650 \mathrm{GHz}$ ); a double-walled, water-cooled steel reaction chamber containing a Broida-type oven and a d.c. discharge electrode; and an InSb bolometer detector. Offset ellipsoidal mirrors are used to direct the radiation through the double pass system and a pathlength modulator is
utilized for baseline smoothing. The radiation is frequency modulated at 25 kHz and is detected at $2 f$ via a lock-in-amplifier.

The CoCN radical was synthesized by the reaction of cobalt vapor, produced in a Broida-type oven, with cyanogen gas. Initially $15-20$ mtor of $(\mathrm{CN})_{2}$ were passed into the reaction chamber from underneath the oven. However, unlike in our previous syntheses of transition metal cyanides, more intense signals were observed if the reactant gas entered through a steel tube over the top of the Broida oven. In both cases, neither a d.c. discharge or a carrier gas such as Ar were found to improve the intensity of the rotational transitions. In order to produce $\mathrm{Co}^{13} \mathrm{CN}, \mathrm{H}^{13} \mathrm{CN}$ was substituted for cyanogen. $\mathrm{H}^{13} \mathrm{CN}$ was synthesized in our lab by the slow reaction of an aqueous solution of $\mathrm{Na}^{13} \mathrm{CN}$ with $\mathrm{H}_{2} \mathrm{SO}_{4}$. The $\mathrm{H}^{13} \mathrm{CN}$ was then distilled, passed through $\mathrm{CaSO}_{4}$ and $\mathrm{P}_{2} \mathrm{O}_{5}$ drying traps, and collected in a liquid nitrogen cooled trap. As for the main isotopomer, $10-15$ mtorr of $\mathrm{H}^{13} \mathrm{CN}$ and no carrier gas were added over the top of the oven; however, a d.c. discharge of 0.2 A at 200 V was required in order to observe rotational transitions of $\mathrm{Co}^{13} \mathrm{CN}$.

Final transition frequencies of CoCN and $\mathrm{Co}^{13} \mathrm{CN}$ were obtained by averaging two scans, one in decreasing and the other in increasing frequency, each 5 MHz in width. For the weaker features, up to five scan pairs were found to be necessary. Each line was fit to a Gaussian profile, in order to determine the center frequency. Typical line widths ranged from 800 kHz at 350 GHz to 1400 kHz at 500 GHz .

## III. Results

Because no previous spectroscopic information existed for CoCN , an extensive search in frequency space, $\sim 30 \mathrm{GHz}$, was conducted in order to locate pure rotational transitions arising from this molecule. During this search a weak octet that was
attributed to an open shell molecule containing cobalt ( $I=7 / 2$ ) was observed. Additional harmonically related octets were found to require integer quantum numbers, indicating an odd spin multiplicity of $S \geq 1$. ( $\mathrm{S}=0$ can be effectively ruled out as the only hyperfine spliting in this case arises from nuclear quadrupole coupling, which would not result in a pattern of eight nearly equally spaced lines.[24]) The B value ( $\sim 4 \mathrm{GHz}$ ) obtained for this set of octets was found to be similar to those of the other transition metal cyanides. Therefore, these features were attributed to CoCN . In total eight groups of harmonically related octets were observed.

Based on similar cobalt radicals, $\operatorname{CoH}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right), \operatorname{CoF}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$, and $\left.\mathrm{CoCl(X} \mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ [19-22] the ground state of CoCN was first assumed to be ${ }^{3} \Phi_{\mathrm{i}}$. In this term, three fine structure components arise, as a result of spin-orbit coupling, per rotational transition, labeled by $\Omega$, where $\Omega=\Lambda+\Sigma$. In an inverted state, the $\Omega=4$ spin-orbit sub-level lies lowest in energy. Cobalt possess one isotope, ${ }^{59} \mathrm{Co}$, with a nuclear spin of $\mathrm{I}=7 / 2$. This nuclear spin angular momentum can further couple to the rotational angular momentum, J, resulting in an octet $(J=I+F)$ for each of the three spin-orbit components within a rotational transition.

The most intense group of eight lines observed for CoCN was assigned as the $\Omega=$ 4 spin-orbit component. In a ${ }^{3} \Phi$ state, lambda-doubling interactions are possible, although expected to be very small in magnitude. The only molecule with a $\Phi$ ground state in which A -doubling has been observed is CoH [17], however the effect was only resolvable in the $\Omega=3$ spin-component, not $\Omega=4$. For $\operatorname{CoCN}$, rotational transitions of comparable intensity to the $\Omega=4$ sub-level were not found to exist. The absence of
lambda-doubling indicates that the ground state of CoCN has a high value of angular momentum, which supports a ${ }^{3} \Phi_{i}$ assignment

In addition to the three spin-orbit components, rotational transitions arising from the vibrational energy levels of CoCN are possible. Based on the previous spectroscopic studies of $\mathrm{ZnCN}, \mathrm{CuCN}$, and NiCN [11,12,14], the bending mode ( $\mathrm{v}_{2}$ ) is sufficiently low in energy $\left(\sim 200-300 \mathrm{~cm}^{-1}\right)$ to populate the rotational energy levels within these states. and is most likely the case for $\operatorname{CoCN}$. For a linear triatomic molecule in a ${ }^{3} \Phi$ state, the bending vibrational levels are subject to Renner-Teller coupling.[25,26] In this phenomenon, the bending vibrational, $l$, and electron orbital angular momenta couple to form $K,(l+\Lambda=K)$ with components labeled by $K_{P}(K+\Sigma=P)$. In a ${ }^{3} \Phi$ state, for the $v_{2}$ $=1$ level, two Renner components result, ${ }^{3}{ }^{3}$ and ${ }^{3} \Delta$, and for the $v_{2}=2$ state three arise, ${ }^{3} \mathrm{H},{ }^{3} \Phi$, and ${ }^{3} \Pi$, all within each of the three spin-orbit sub-levels. In addition, rotational transitions arising from the metal carbon stretch have also been observed for ZnCN [11] and NiCN[14] and therefore may be present in the rotational spectrum of CoCN .

A set of two octets of similar intensity were observed approximately 2 and 3 GHz to higher frequency of the $\Omega=4$ spin-orbit component, respectively. In $\mathrm{ZnCN}, \mathrm{CuCN}$, and NiCN , rotational transitions arising from the $\mathrm{v}_{2}=1$ mode were found to be located at a similar frequency spacing from the ground state.[11,12,14] As a result, these octets were assigned as the two before mentioned Remer-components of the $v_{2}=1$ level of the ${ }^{3} \Phi_{4}$ spin-component. The two components do not exhibit any evidence of P-type doubling as was observed in the ${ }^{2} \Pi_{3 / 2}, v_{2}=1$ vibronic component in NiCN. Again this suggests a high value of orbital angular momentum for the ground state. A larger hyperfine spacing between the eight components of the lower frequency octet was
observed; therefore, it was assigned as the ${ }^{3} \Gamma_{5}$ vibronic component and the other as the ${ }^{3} \Delta_{3}$ level. Two additional weak octets were observed approximately $5-6 \mathrm{GHz}$ higher in frequency. These presumably are two of the Renner components of the $v_{2}=2$ vibronic level, most likely ${ }^{3} \mathrm{H}_{6}$ and ${ }^{3} \Pi_{2}$. The missing component is most likely the ${ }^{3} \Phi_{4}$, shifted by Fermi resonance with the first quantum of the metal-carbon stretch $\left(v_{1}\right)$, which has the same $P$ value.

Between the $\Omega=4$ spin-orbit component and the $v_{2}=1$ vibronic sub-levels, three additional weak octets were observed. The first octet was found to be close in frequency to the ground state line, $\sim 100 \mathrm{MHz}$ higher in the $\mathrm{J}=45 \leftarrow 44$ rotational transition. The $B$ value for this octet was smaller than that for the ground state; however at higher J, the small value of the centrifugal distortion constants results in this feature moving to higher frequency of the $\Omega=4$ spin-orbit component. Interestingly, the hyperfine splitting in this octet is very similar to the ground state. The hyperfine spacing between the eight components of the ground state octet and the metal-ligand stretching modes are expected be similar, as has been observed for CoCl [22] As a result, this weak octet was tentatively assigned as the $\mathrm{v}_{1}=1\left({ }^{3} \Phi_{4}\right)$ metal-carbon stretch. The appearance of the rotational transitions of the stretch to higher frequency than the ground state suggests that this state is perturbed. This perturbation is most likely the result of Fermi resonance with the $v_{2}=2\left({ }^{3} \Phi_{4}\right)$ component of the bending mode. In NiCN, a strong Fermi resonance was observed.[13] This interaction results in the in the partial mixing of the rotational constants of the two perturbing states. In this case, the $v_{2}=2\left({ }^{3} \Phi_{4}\right)$ sub-level is expected to be shifted closer in frequency to the ground state. However, most likely because of this and the weak nature of the $\mathrm{v}_{2}=2$ vibronic components it was not observed.

Of the two remaining octets, the one located approximately 600 MHz higher in frequency than the ground state spin-component was the second most intense line observed. For CoH , the energy separation between the $\Omega=4$ and 3 spin-components has been measured.[27] Based on this, the spin-orbit constant, $A$, was calculated to be $221.5 \mathrm{~cm}^{-1}$ [17]. The electronic structure of $\operatorname{NiCN}\left(\mathrm{X}^{2} \mathrm{~A}_{\mathrm{i}}\right)$ [13,14] was found to be quite similar to $\mathrm{NiH}\left(\mathrm{X}^{2} \Delta_{\mathrm{i}}\right)$ [28], suggesting that the spin-orbit interaction in CoCN might be similar to CoH . Assuming this case, the energy separation between the spin-components of CoCN is expected to be large $\sim 700 \mathrm{~cm}^{-1}$. Using the approximate relationship ( $\mathrm{B}_{\Omega}=$ $\mathrm{B}(1+2 \mathrm{~B} \mathrm{\Sigma} / \mathrm{AA}))[29]$, the two additional spin-components should be found close in frequency to the ground state octet $(\Omega=4)$, as in NiCN . It may be argued that CoCN , contrary to $\mathrm{NiCN}[13,14]$ behaves more like CoF; however, the $A$ value of CoF is -232 $\mathrm{cm}^{-1}[20]$, which is nearly the same as for CoH . Therefore, this second strongest line was assigned as the $\Omega=3$ spin-orbit component. The final octet, which is less intense than the $\Omega=3$ spin-level was assigned as the $\Omega=2$ spin-component.

Figure 1 illustrates a stick spectrum of the observed octets of the $J=45 \leftarrow 44$ rotational transition near 379 GHz of CoCN . Each octet is represented as a single feature with its approximate relative intensity, labeled as $\mathrm{K}_{\mathrm{p}}$. The strongest line belongs to the $\Omega$ $=4$ spin-orbit component; the $\Omega=3$ and 2 sub-levels are located approximately 600 MHz and 1.2 GHz higher in frequency, respectively. The octet $\sim 100 \mathrm{MHz}$ higher in frequency of the ground state is the tentatively assigned $v_{1}=1\left({ }^{3} \Phi_{4}\right)$ stretch. The $v_{2}=1$ vibronic Renner components, ${ }^{3} \Gamma_{s}$ and ${ }^{3} \Delta_{3}$, are shown $\sim 2 \mathrm{GHz}$ higher in frequency than the ground state line. The $\mathrm{v}_{2}=2$ vibronic components are also shown, however due to their poor intensity the hyperfine structure could not be well resolved in this work.

Figure 2 show a laboratory spectrum of the $\Omega=4,3$, and 2 spin-components of the $\mathrm{J}=45 \leftarrow 44$ rotational transition in the 378 GHz region. For each sub-level the hyperfine spliting due to the ${ }^{59} \mathrm{Co}$ nucleus is clearly resolved. All three spin-orbit components are shown with a frequency break of $\sim 500 \mathrm{MHz}$ between each.

The measured rotational transition frequencies for the spin-orbit components of the $\mathrm{X}^{3} \Phi_{\mathrm{i}}$ state of CoCN are listed in Table 1. Eleven, five, and three rotational transitions were recorded in the $\Omega=4,3$, and 2 sub-levels respectively. Hyperfine splittings due to the ${ }^{59} \mathrm{Co}$ nucleus were resolved for each rotational transition.

The measured rotational transitions for the vibronic levels of CoCN can be found in EPAPS.[30] For the $v_{2}=1$ level, nine rotational transitions were recorded in each Renner component $\left({ }^{3} \Gamma_{s}\right.$ and $\left.{ }^{3} \Delta_{3}\right)$. For the $v_{1}=1\left({ }^{3} \Phi_{4}\right)$ metal carbon stretch, three rotational transitions were measured in each. In all cases, ${ }^{59} \mathrm{Co}$ hyperfine splittings were resolved in each rotational transition.

In order to establish the molecular geometry of cobalt cyanide, measurement of rotational transitions arising from at least one additional isotopomer were required. Unfortunately, cobalt has only one stable isotope, ${ }^{59} \mathrm{Co}$; therefore, the only other isotopomers that could be observed were either ${ }^{13} \mathrm{C}$ or ${ }^{15} \mathrm{~N}$. Searches for signals arising from these species in natural abundance were unsuccessful; not surprisingly due to the low intensity of the rotational transitions observed for the main isotopomer. As a result, $\mathrm{H}^{13} \mathrm{CN}$ was used to synthesize $\mathrm{C}{ }^{13} \mathrm{CN}$. Rotational transitions with nearly the same hyperfine splitting as the ground state of the main isotopomer were observed for $\mathrm{Co}^{13} \mathrm{CN}$ and were assigned as the $\Omega=4$ spin-component. A laboratory spectrum of the $J=48 \leftarrow$ 47 rotational transition of $\mathrm{Co}^{13} \mathrm{CN}$ is shown in Figure 3. The signal to noise ratio
observed for this octet is low; however, eight individual features are clearly present in the highlighted region. In total four rotational transitions arising from $\mathrm{Co}^{13} \mathrm{CN}$ were measured for the $\Omega=4$ spin-orbit component and are listed in Table 2 . From the rotational constant determined for this isotopomer, the structure of CoCN was determined to be linear cyanide.

## IV. Analysis

The pure rotational transitions of $\operatorname{CoCN}\left(X^{3} \Phi_{i}\right)$ were fit to the following effective Hamitonian in a case ( $a_{\beta}$ ) basis [17,31]

$$
\begin{equation*}
\hat{H}_{\mathrm{eff}}=\hat{\mathrm{H}}_{\mathrm{Rot}}+\hat{\mathrm{H}}_{\mathrm{so}}+\hat{\mathrm{H}}_{\mathrm{ss}}+\hat{\mathrm{H}}_{\mathrm{MAF}} \tag{1}
\end{equation*}
$$

which contains rotational, spin-orbit, spin-spin, and magnetic hyperfine terms. The results of the least squares fit of Eq. (1) to the rotational data are shown in Table 3. Because rotational transitions recorded for CoCN contained high I values, three centrifugal distortion terms, $D, H$, and $L$ were found to be necessary in the analysis. For COCN , the value of $A$, the spin-orbit constant, was fixed to that of CoH .[17] Also, the spin-spin parameter, $\lambda$, was fixed to zero. For both constants, centrifugal distortion parameters up to second order were found to be necessary. The magnetic hyperfine constants, $a$ and $b+c$ were also utilized. Unfortunately, the value of the isolated $b$ constant could not be reliably established from this data set. A value for the electric quadrupole parameter, eq0Q, was also not determinable. The $h_{3 D}$ parameter, introduced to account for systematic trends in the residuals of the LMR data in the $\Omega=3$ level of CoH was also found to be necessary[17]. Assignment of the F quantum numbers was made by fitting the rotational data with the quantum numbers for each octet as in Table 1 and in reverse order. For the reverse assignment, the rms was $>600 \mathrm{kHz}$ and the value of $a$ was
negative. The overall rms of the final fit is 144 kHz , less than the estimated experimental accuracy of indicating the data was relatively well modeled by this Hamiltonian.

Rotational transitions arising from the various vibronic components as well as the $\Omega=4,3$, and 2 spin-orbit sub-levels were fit using an effective Hamiltonian. In this expression the hyperfine splittings were modeled using the diagonal elements of the magnetic hyperfine Hamiltonian[20] as well as a centrifugal distortion term given as[17]

$$
\begin{equation*}
h_{\Omega D}=h_{\Omega} \cdot R^{2} \tag{2}
\end{equation*}
$$

An effective approach could only be employed for the vibronic components, as the Renner-Teller effect has not been considered in the same detail for $\Phi$ states as it has been for $\Delta$ and $\Pi$ states.[25,26] The large frequency separation ( $>1 \mathrm{GHz}$ ) observed in the Renner-Teller components of the $v_{2}=1$ and $v_{2}=2$ vibronic levels suggests that this interaction is substantial in CoCN . The results of the fits for each sub-level are listed in Table 4. In the case of the vibronic components, the value of P was substituted for $\Omega$. For each component, the rms values are below 100 kHz , indicating that these expressions adequately modeled the data.

## Y. Discussion

## A. Structure and Bonding

From the rotational transition data measured for CoCN and its isotopomer $\mathrm{Co}^{13} \mathrm{CN}$, this radical was found to possess a linear cyanide structure. As a result, the lower energy isomer of CoCN exhibits the same geometry as the 3 d transition metal cyanides of nickel, copper, and zinc, [11-14] rather than the isocyanide form like iron.[10]

The $\mathrm{r}_{0}$ bond lengths determined for CoCN are shown in Table 5. Because only rotational transitions arising from the $\Omega=4$ spin-orbit component were observed for the
$\mathrm{Co}^{13} \mathrm{CN}$ isotopomer, a structure based only on this sub-level could be determined. For cobalt cyanide, the ros=4 metal-carbon bond length is $1.8827(7) \AA$ and the CN bond length is $1.1313(10) \AA$. The metal-carbon bond length is longer for CoCN than for either NiCN or CuCN . This result is contrary to the $\mathrm{CoC}\left(\mathrm{X}^{2} \Sigma^{+}\right) \mathrm{r}_{0}=1.5612 \AA$ bond length, which is significantly shorter compared to that of $\mathrm{NiC}\left(\mathrm{X}^{1} \Sigma^{+}\right) \mathrm{r}_{0}=1.6308 \AA$ [32]. In CuCN and NiCN , the metal-carbon bond lengths are similar: most likely due to the removal of a $\delta$ non-bonding electron between the CuCN and Ni CN electron
configurations.[14] The ${ }^{3} \Phi$ ground state of CoCN arises from a $\delta \pi$ configuration, which corresponds to removal of a $\pi$ electron from the NiCN electron configuration. This $\pi$ orbital is largely antibonding in character; removal of an electron from it would be expected to decrease the metal carbon bond length. This appears to be contrary to the experimental observations. However, the experimentally determined bond lengths for CoCN may be misleading since they are based solely on data from the $\Omega=4$ spincomponent for the two isotopomers. The $\mathrm{B}_{\Omega=4}$ value should be smaller than the overall mechanical B (derived from all three spin-components) of the molecule.[25] A more accurate $r_{0}$ structure could be obtained if this $B$ is used, unfortunately it is not available for $\mathrm{C}^{13} \mathrm{CN}$. CoCN possesses the shortest CN bond length of any of the transition metal cyanides. Because rotational transitions of only two isotopomers were recorded, $\mathrm{r}_{5}, \mathrm{r}_{\mathrm{m}}{ }^{(1)}$, and $r_{m}{ }^{(2)}$ structures could not be determined. [33,34] The elongated metal-carbon bond length and shortened CN bond length may be the result of zero-point perturbations, which have been observed in the $r_{0}$ structure of $\ln C N\left(r_{0} C N=1.135(11) \AA\right.$ as opposed to $\left.\mathrm{r}_{\mathrm{m}}{ }^{(2)} \mathrm{CN}=1.1472 \AA\right) \cdot[6]$ These methods have been found to better approximate an equilibrium geometry, thereby removing any zero-point anomalies.

The preference for cobalt to form the linear cyanide structure suggests that the metal ligand bond also has a significant covalent character as has been postulated for nickel, copper, and zinc cyanides.[11-14] The linear cyanide structure is believed to occur for these species as a result of $d-\pi^{*}$ back bonding from the metal to the ligand. [11,14] The bonding preference to the carbon atom arises because the $\pi^{*}$ orbitals of CN have a slightly greater carbon character. As one moves further to the left on the periodic table in the 3d transition metal row, the number of delectrons decreases. Evidently cobalt must have sufficient d-electron density to continue this back donating behavior and form the cyanide structure.

The relative strengths of the M-C bonds can also be probed via the Kratzer relationship. For $\mathrm{NiCN}, \mathrm{CuCN}$, and ZnCN , the metal-carbon stretching frequencies have been estimated as $491 \mathrm{~cm}^{-1}, 478 \mathrm{~cm}^{-1}$ and $418 \mathrm{~cm}^{-1}$ respectively.[11,12,14] For CoCN, the value of $\omega_{1}$ is $426 \mathrm{~cm}^{-1}$, which is closest to the value found for ZnCN . The low value of $\omega_{1}$ suggests that the metal carbon bond is much weaker in CoCN than in NiCN and CuCN , which is supported further by the lengthened metal-carbon bond compared to the other two cyanides.

## B. Cobalt Hyperfine Interactions

As mentioned previously, the ${ }^{3} \Phi_{i}$ ground state of CoCN arises from a $\delta \pi$ electron configuration. The magnetic hyperfine interactions that arise for CoCN include electron orbital- nuclear-spin, $a$, and electron spin - nuclear spin, $(b+c)$. The second interaction can be divided into two contributions, the Fermi contact term, $b_{F}\left(\mathrm{~b}_{\mathrm{F}}=\mathrm{b}+1 / 3 \mathrm{c}\right)$ and $c$, the dipolar term. The value of the Fermi contact term depends on the unpaired electron
density at the nucleus with spin and contributions to the $c$ term arise from the anisotropic unpaired electron distribution at that nucleus. [24]

In a $\delta \pi$ configuration the magnitude of the $b_{F}$ parameter should be close to zero as no unpaired $\sigma$ electrons are present. In fact for CoH this parameter has been measured to be only $-15.9(86) \mathrm{MHz}$.[17] Unfortunately because $b$ could not be fit for CoCN , the value of $b_{F}$ could not be obtained. As has been discussed for CoH , the majority of the magnetic hyperfine coupling will manifest then itself in the $a$ and $c$ parameters. For CoCN , the value of the $a$ constant was found to be greater than $b+c(829.9 \mathrm{vs} .-736 \mathrm{MHz}$ ) as was found for CoH ( $621.01 \mathrm{vs} . ~-320.08 \mathrm{MHz}$ [17]). For cobalt atom, the value of $a$ has been measured as 617.9 MHz for the $3 \mathrm{~d}^{8} 4 \mathrm{~s}^{1}$ configuration and 702.8 MHz for the $3 \mathrm{~d}^{7}$ $4 s^{2}$ configuration.[35] In $\mathrm{CoCN}, a$ compares quite similarly to that of cobalt atom.

A comparison of the hyperfine parameters of $\mathrm{CoF}, \mathrm{CoCl}$ and CoCN can also be made[18,20]. Unfortunately, for CoF and CoCl only the $\Omega=4$ spin-orbit component of the ground state has been observed. Because hyperfine splittings were resolved in this sub-level a value of $h_{\Omega=4}$ was obtained. The value of $h_{\Omega=4}$ for CoF is $974.9(18) \mathrm{GHz}$ [18] and for CoCl is $1318(16) \mathrm{GHz}$, [20]. The value of $\mathrm{h}_{8 \times 4}$ is $1754.0(5.8) \mathrm{GHz}$ for CoCN , which compares more closely to that of CoCl than CoF . This suggests that the electronic structure of $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ may have some similarity to $\mathrm{CoCl}\left(\mathrm{X}^{3} \Phi_{i}\right)$ unilike $\mathrm{NiCN}\left(\mathrm{X}^{2} \Delta_{i}\right)[13,14]$, which is quite different from $\mathrm{NiF}\left(\mathrm{X}^{2} \Pi_{i}\right)$ and $\mathrm{NiCl}\left(\mathrm{X}^{2} \Pi_{i}\right)[36,37]$. This may mean a greater ionic character in the cobalt-cyanide bond than exist for nickel, copper, and zinc cyanides.


#### Abstract

V1. Conclusion The pure rotational spectrum of CoCN has been observed using direct absorption millimeter/sub-millimeter wave techniques, which is the first spectroscopic observation of this radical by any means. Rotational transitions of CoCN in all three spin-orbit components and in the $\Omega=4$ of the isotopomer, $\mathrm{Co}^{13} \mathrm{CN}$, have been recorded. From this data, the structure of CoCN has been determined unambiguously to be linear cyanide. This geometry is the same as has been observed for nickel, copper, and zinc cyanides, suggesting that the cobalt and cyanide bond has significant covalent character. Within each rotational transition, hyperfine splittings arising from the ${ }^{59} \mathrm{Co}(\mathrm{I}=7 / 2)$ nucleus were observed. The magnetic hyperfine constants determined from the global fit of the rotational transitions of Co CN are consistent with a $\pi \delta$ electron configuration and are similar to those measured for CoH . The value of the $h_{\Omega}=4$ parameter for CoCN is similar to that of CoCl suggesting an increased ionic character in CoCN compared to the other transition metal cyanides.


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Table 1. Measured Rotational Transition Frequencies for $\left.\operatorname{CoCN}\left(X^{3} \Phi_{i}\right)(\Omega=4 \text { and } 3)^{2}\right)$

| $\Omega$ | J | $\mathrm{F}^{\text {i }}$ | $\leftarrow$ | J" | $F^{\text {r }}$ | $\nu_{\text {obs }}$ | $\nu_{\text {obs }}$ - $V_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | 42 | 38.5 |  | 41 | 37.5 | 352544.087 | 0.050 |
| 4 | 42 | 39.5 |  | 41 | 38.5 | 352540.703 | 0.030 |
| 4 | 42 | 40.5 |  | 41 | 39.5 | 352537.161 | 0.026 |
| 4 | 42 | 41.5 |  | 41 | 40.5 | 352533.409 | -0.015 |
| 4 | 42 | 42.5 |  | 41 | 41.5 | 352529.544 | 0.002 |
| 4 | 42 | 43.5 |  | 41 | 42.5 | 352525.470 | -0.021 |
| 4 | 42 | 44.5 |  | 41 | 43.5 | 352521.268 | -0.004 |
| 4 | 42 | 45.5 |  | 41 | 44.5 | 352516.860 | -0.027 |
| 4 | 44 | 40.5 |  | 43 | 39.5 | 369292.944 | 0.033 |
| 4 | 44 | 41.5 |  | 43 | 40.5 | 369289.854 | 0.029 |
| 4 | 44 | 42.5 |  | 43 | 41.5 | 369286.496 | -0.091 |
| 4 | 44 | 43.5 |  | 43 | 42.5 | 369283.111 | -0.089 |
| 4 | 44 | 44.5 |  | 43 | 43.5 | 369279.584 | -0.080 |
| 4 | 44 | 45.5 |  | 43 | 44.5 | 369275.907 | -0.074 |
| 4 | 44 | 46.5 |  | 43 | 45.5 | 369272.077 | -0.074 |
| 4 | 44 | 47.5 |  | 43 | 46.5 | 369268.131 | -0.046 |
| 3 | 44 | 40.5 |  | 43 | 39.5 | 369890.716 | 0.069 |
| 3 | 44 | 41.5 |  | 43 | 40.5 | 369888.309 | -0.137 |
| 3 | 44 | 42.5 |  | 43 | 41.5 | 369885.979 | -0.118 |
| 3 | 44 | 43.5 |  | 43 | 42.5 | 369883.590 | -0.013 |
| 3 | 44 | 44.5 |  | 43 | 43.5 | 369881.158 | 0.192 |
| 3 | 44 | 45.5 |  | 43 | 44.5 | 369878.432 | 0.243 |
| 3 | 44 | 46.5 |  | 43 | 45.5 | 369875.608 | 0.334 |
| 3 | 44 | 47.5 |  | 43 | 46.5 | 369872.734 | 0.509 |
| 4 | 45 | 41.5 |  | 44 | 40.5 | 377665.296 | 0.042 |
| 4 | 45 | 42.5 |  | 44 | 41.5 | 377662.352 | 0.058 |
| 4 | 45 | 43.5 |  | 44 | 42.5 | 377659.172 | -0.021 |
| 4 | 45 | 44.5 |  | 44 | 43.5 | 377655.958 | 0.006 |
| 4 | 45 | 45.5 |  | 44 | 44.5 | 377652.501 | -0.071 |
| 4 | 45 | 46.5 |  | 44 | 45.5 | 377649.039 | -0.015 |
| 4 | 45 | 47.5 |  | 44 | 46.5 | 377645.354 | -0.045 |
| 4 | 45 | 48.5 |  | 44 | 47.5 | 377641.520 | -0.089 |
| 3 | 45 | 41.5 |  | 44 | 40.5 | 378264.251 | -0.024 |
| 3 | 45 | 42.5 |  | 44 | 41.5 | 378262.089 | -0.118 |
| 3 | 45 | 43.5 |  | 44 | 42.5 | 378259.865 | -0.136 |
| 3 | 45 | 44.5 |  | 44 | 43.5 | 378257.587 | -0.073 |
| 3 | 45 | 45.5 |  | 44 | 44.5 | 378255.167 | -0.018 |
| 3 | 45 | 46.5 |  | 44 | 45.5 | 378252.409 | -0.170 |
| 3 | 45 | 47.5 |  | 44 | 46.5 | 378249.863 | 0.019 |
| 3 | 45 | 48.5 |  | 44 | 47.5 | 378247.097 | 0.113 |
| 2 | 45 | 41.5 |  | 44 | 40.5 | 378792.706 | 0.125 |
| 2 | 45 | 42.5 |  | 44 | 41.5 | 378790.129 | 0.161 |
| 2 | 45 | 43.5 |  | 44 | 42.5 | 378787.525 | 0.267 |

Table 1. Cont'd.

| $\Omega$ | $J$ | $F$ | $\leftarrow$ | $J^{\prime \prime}$ | $F^{\prime \prime}$ | $v_{\text {obs }}$ | $v_{\text {obs }} V_{\text {calc }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | ---: |
| 2 | 45 | 44.5 |  | 44 | 43.5 | 378784.768 | 0.314 |
| 2 | 45 | 45.5 |  | 44 | 44.5 | 378781.733 | 0.173 |
| 2 | 45 | 46.5 |  | 44 | 45.5 | 378778.519 | -0.061 |
| 2 | 45 | 47.5 |  | 44 | 46.5 | 378775.310 | -0.208 |
| 2 | 45 | 48.5 |  | 44 | 47.5 | 378771.813 | -0.566 |
| 4 | 46 | 42.5 |  | 45 | 41.5 | 386036.199 | 0.065 |
| 4 | 46 | 43.5 |  | 45 | 42.5 | 386033.330 | 0.038 |
| 4 | 46 | 44.5 |  | 45 | 43.5 | 386030.293 | -0.026 |
| 4 | 46 | 45.5 |  | 45 | 44.5 | 386027.388 | 0.174 |
| 4 | 46 | 46.5 |  | 45 | 45.5 | 386023.957 | -0.023 |
| 4 | 46 | 47.5 |  | 45 | 46.5 | 386020.713 | 0.097 |
| 4 | 46 | 48.5 |  | 45 | 47.5 | 386017.119 | -0.006 |
| 4 | 46 | 49.5 |  | 45 | 48.5 | 386013.470 | -0.037 |
| 3 | 46 | 43.5 |  | 45 | 42.5 | 386633.546 | -0.120 |
| 3 | 46 | 44.5 |  | 45 | 43.5 | 386631.520 | -0.075 |
| 3 | 46 | 45.5 |  | 45 | 44.5 | 386629.173 | -0.223 |
| 3 | 46 | 46.5 |  | 45 | 45.5 | 386626.782 | -0.291 |
| 3 | 46 | 47.5 |  | 45 | 46.5 | 386624.393 | -0.234 |
| 3 | 46 | 48.5 |  | 45 | 47.5 | 386622.010 | -0.050 |
| 2 | 46 | 42.5 |  | 45 | 41.5 | 387181.599 | -0.381 |
| 2 | 46 | 43.5 |  | 45 | 42.5 | 387179.317 | -0.157 |
| 2 | 46 | 44.5 |  | 45 | 43.5 | 387176.997 | 0.120 |
| 2 | 46 | 45.5 |  | 45 | 44.5 | 387174.311 | 0.119 |
| 4 | 47 | 43.5 |  | 46 | 42.5 | 394405.513 | 0.016 |
| 4 | 47 | 44.5 |  | 46 | 43.5 | 394402.848 | 0.080 |
| 4 | 47 | 45.5 |  | 46 | 44.5 | 394399.913 | -0.001 |
| 4 | 47 | 46.5 | 46 | 45.5 | 394396.945 | 0.007 |  |
| 4 | 47 | 47.5 |  | 46 | 46.5 | 394393.861 | 0.021 |
| 4 | 47 | 48.5 | 46 | 47.5 | 394390.630 | 0.009 |  |
| 4 | 47 | 49.5 |  | 46 | 48.5 | 394387.389 | 0.107 |
| 4 | 47 | 50.5 | 46 | 49.5 | 394383.756 | -0.068 |  |
| 3 | 47 | 43.5 |  | 46 | 42.5 | 395004.754 | 0.176 |
| 3 | 47 | 44.5 |  | 46 | 43.5 | 395002.705 | -0.049 |
| 3 | 47 | 45.5 |  | 46 | 44.5 | 395000.745 | -0.063 |
| 3 | 47 | 46.5 |  | 46 | 45.5 | 394998.547 | -0.197 |
| 3 | 47 | 47.5 |  | 46 | 46.5 | 394996.370 | -0.193 |
| 3 | 47 | 48.5 |  | 46 | 47.5 | 394994.111 | -0.155 |
| 3 | 47 | 49.5 |  | 46 | 48.5 | 394991.628 | -0.229 |
| 3 | 47 | 50.5 |  | 46 | 49.5 | 394989.202 | -0.135 |
| 4 | 48 | 44.5 |  | 47 | 43.5 | 402773.318 | 0.025 |
| 4 | 48 | 45.5 |  | 47 | 44.5 | 402770.665 | -0.004 |
| 4 | 48 | 46.5 |  | 47 | 45.5 | 402767.967 | 0.038 |
|  |  |  |  |  |  |  |  |

Table 1. Cont'd.

| $\Omega$ | $J$ | $F$ | $\leftarrow$ | $J^{\prime \prime}$ | $F^{\prime \prime}$ | $V_{\text {obs }}$ | $V_{\text {obss }} V_{\text {calk }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | 48 | 47.5 |  | 47 | 46.5 | 402765.112 | 0.039 |
| 4 | 48 | 48.5 |  | 47 | 47.5 | 402762.047 | -0.056 |
| 4 | 48 | 49.5 |  | 47 | 48.5 | 402759.062 | 0.043 |
| 4 | 48 | 50.5 |  | 47 | 49.5 | 402755.854 | 0.031 |
| 4 | 48 | 51.5 |  | 47 | 50.5 | 402752.541 | 0.026 |
| 3 | 48 | 44.5 |  | 47 | 43.5 | 403371.593 | 0.479 |
| 3 | 48 | 45.5 |  | 47 | 44.5 | 403369.656 | 0.256 |
| 3 | 48 | 46.5 |  | 47 | 45.5 | 403367.760 | 0.186 |
| 3 | 48 | 47.5 |  | 47 | 46.5 | 403365.715 | 0.080 |
| 3 | 48 | 48.5 |  | 47 | 47.5 | 403363.705 | 0.118 |
| 3 | 48 | 49.5 |  | 47 | 48.5 | 403361.399 | -0.032 |
| 3 | 48 | 50.5 |  | 47 | 49.5 | 403359.240 | 0.071 |
| 3 | 48 | 51.5 |  | 47 | 50.5 | 403356.816 | 0.014 |
| 2 | 48 | 44.5 |  | 47 | 43.5 | 403954.584 | -0.259 |
| 2 | 48 | 45.5 |  | 47 | 44.5 | 403952.289 | -0.243 |
| 2 | 48 | 46.5 |  | 47 | 45.5 | 403950.218 | 0.078 |
| 2 | 48 | 47.5 |  | 47 | 46.5 | 403947.697 | 0.025 |
| 2 | 48 | 48.5 |  | 47 | 47.5 | 403945.270 | 0.140 |
| 2 | 48 | 49.5 |  | 47 | 48.5 | 403942.701 | 0.184 |
| 2 | 48 | 50.5 |  | 47 | 49.5 | 403939.963 | 0.126 |
| 2 | 48 | 51.5 |  | 47 | 50.5 | 403937.134 | 0.042 |
| 4 | 55 | 51.5 |  | 54 | 50.5 | 461299.671 | 0.056 |
| 4 | 55 | 52.5 |  | 54 | 51.5 | 461297.528 | -0.056 |
| 4 | 55 | 53.5 |  | 54 | 52.5 | 461295.349 | -0.127 |
| 4 | 55 | 54.5 |  | 54 | 53.5 | 461293.307 | 0.016 |
| 4 | 55 | 55.5 |  | 54 | 54.5 | 461290.976 | -0.054 |
| 4 | 55 | 56.5 |  | 54 | 55.5 | 461288.754 | 0.061 |
| 4 | 55 | 57.5 | 54 | 56.5 | 461286.410 | 0.128 |  |
| 4 | 55 | 58.5 | 54 | 57.5 | 461283.775 | -0.021 |  |
| 4 | 56 | 52.5 | 55 | 51.5 | 469652.998 | -0.003 |  |
| 4 | 56 | 53.5 | 55 | 52.5 | 469650.875 | -0.162 |  |
| 4 | 56 | 54.5 | 55 | 53.5 | 469648.942 | -0.059 |  |
| 4 | 56 | 55.5 |  | 55 | 54.5 | 469646.848 | -0.044 |
| 4 | 56 | 56.5 |  | 55 | 55.5 | 469644.723 | 0.011 |
| 4 | 56 | 57.5 |  | 55 | 56.5 | 469642.484 | 0.025 |
| 4 | 56 | 58.5 |  | 55 | 57.5 | 469640.237 | 0.101 |
| 4 | 56 | 59.5 |  | 55 | 58.5 | 469637.788 | 0.045 |
| 4 | 57 | 53.5 |  | 56 | 52.5 | 478004.367 | 0.016 |
| 4 | 57 | 54.5 |  | 56 | 53.5 | 478002.351 | -0.101 |
| 4 | 57 | 55.5 |  | 56 | 54.5 | 478000.399 | -0.085 |
| 4 | 57 | 56.5 |  | 56 | 55.5 | 477998.480 | 0.032 |
| 4 | 58 | 54.5 |  | 57 | 53.5 | 486353.626 | 0.012 |
| 4 | 58 | 55.5 |  | 57 | 54.5 | 486351.688 | -0.089 |
|  |  |  |  |  |  |  |  |

Table 1. Cont'd.

| $\Omega$ | $J$ | $\mathrm{~F}^{\prime}$ | $\leftarrow$ | $J^{\prime \prime}$ | $\mathrm{F}^{\prime \prime}$ | $V_{\text {obs }}$ | $V_{\text {obs }} \mathrm{V}_{\text {caic }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 4 | 58 | 56.5 |  | 57 | 55.5 | 486349.790 | -0.084 |
| 4 | 58 | 57.5 |  | 57 | 56.5 | 486347.886 | -0.020 |
| 4 | 58 | 58.5 |  | 57 | 57.5 | 486345.889 | 0.015 |
| 4 | 58 | 59.5 |  | 57 | 58.5 | 486343.821 | 0.044 |
| 4 | 58 | 60.5 |  | 57 | 59.5 | 486341.688 | 0.072 |
| 4 | 58 | 61.5 |  | 57 | 60.5 | 486339.441 | 0.049 |
| 4 | 59 | 55.5 |  | 58 | 54.5 | 494700.833 | 0.094 |
| 4 | 59 | 56.5 |  | 58 | 55.5 | 494698.801 | -0.160 |
| 4 | 59 | 57.5 |  | 58 | 56.5 | 494697.062 | -0.058 |
| 4 | 59 | 58.5 |  | 58 | 57.5 | 494695.208 | -0.009 |
| 4 | 59 | 59.5 |  | 58 | 58.5 | 494693.316 | 0.063 |
| 4 | 59 | 60.5 |  | 58 | 59.5 | 494691.242 | 0.014 |
| 4 | 59 | 61.5 |  | 58 | 60.5 | 494689.289 | 0.147 |
| 4 | 59 | 62.5 | 58 | 61.5 | 494687.014 | 0.018 |  |

a) $\ln \mathrm{MHz}$.

Table 2. Measured Rotational Transitions Frequencies for $\mathrm{Co}^{13} \mathrm{CN}\left(\mathrm{X}^{3} \Phi_{1}\right)(\Omega=4)^{\text {a) }}$

| $J$ | $F^{\prime}$ | $\leftarrow$ | $J^{n}$ | $F^{\prime \prime}$ | $v_{\text {obs }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 45 | 41.5 | 44 | 40.5 | 373820.243 | $v_{\text {obs }}-V_{\text {calc }}$ |
| 45 | 42.5 | 44 | 41.5 | 373817.186 | 0.033 |
| 45 | 43.5 | 44 | 42.5 | 373814.177 | 0.118 |
| 45 | 46.5 | 44 | 45.5 | 373803.804 | 0.033 |
| 45 | 47.5 | 44 | 46.5 | 373799.936 | -0.127 |
| 45 | 48.5 | 44 | 47.5 | 373796.283 | 0.064 |
| 46 | 44.5 | 45 | 43.5 | 382100.249 | -0.091 |
| 46 | 45.5 | 45 | 44.5 | 382097.095 | -0.094 |
| 46 | 46.5 | 45 | 45.5 | 382093.825 | -0.082 |
| 46 | 47.5 | 45 | 46.5 | 382090.407 | -0.088 |
| 46 | 48.5 | 45 | 47.5 | 382086.974 | 0.021 |
| 46 | 49.5 | 45 | 48.5 | 382083.326 | 0.043 |
| 47 | 43.5 | 46 | 42.5 | 390390.843 | 0.116 |
| 47 | 48.5 | 46 | 47.5 | 390375.662 | 0.031 |
| 47 | 49.5 | 46 | 48.5 | 390372.278 | 0.034 |
| 47 | 50.5 | 46 | 49.5 | 390368.833 | 0.097 |
| 48 | 44.5 | 47 | 43.5 | 398673.624 | 0.020 |
| 48 | 45.5 | 47 | 44.5 | 398670.931 | -0.010 |
| 48 | 46.5 | 47 | 45.5 | 398668.080 | -0.080 |
| 48 | 50.5 | 47 | 49.5 | 398655.919 | 0.042 |
| 48 | 51.5 | 47 | 50.5 | 398652.460 | -0.061 |

a) In MHz .

Table 3. Spectroscopic Constants for $\left.\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{i}\right)^{2}\right)$

| Parameter | Value (MHz) |
| :---: | :---: |
| B | $4208.661(63)$ |
| D | $0.001363(37)$ |
| H | $-5.18(97) \times 10^{-8}$ |
| L | $1.90(91) \times 10^{-12}$ |
| A | $-6640000^{\mathrm{b}}$ |
| $\mathrm{A}_{\mathrm{D}}$ | $-1.7709(31)$ |
| $\mathrm{A}_{\mathrm{H}}$ | $6.4686(71) \times 10^{-5}$ |
| $\lambda_{\mathrm{D}}$ | $-1.3785(77)$ |
| $\lambda_{\mathrm{H}}$ | $0.0002864(18)$ |
| a | $829.9(9.7)$ |
| $\mathrm{b}+\mathrm{c}$ | $-736(29)$ |
| $\mathrm{h}_{3}$ | $0.348(16)$ |
| rms | 0.144 |

a) Errors are $3 \sigma$ and apply to last places.
b) Held fixed, see text.

Table 4. Effective Spectroscopic Constants of Individual Components for CoCN and $\left.\mathrm{Co}{ }^{13} \mathrm{CN}\left(\mathrm{X}^{3} \Phi_{1}\right)^{4}\right)$

| Parameter | $\mathrm{v}=0\left(^{3} \Phi_{4}\right)$ | $v=0\left({ }^{3} \Phi_{3}\right)$ | $v=0\left({ }^{3} \Phi_{2}\right)$ | $v_{2}=1\left({ }^{3} \Delta_{3}\right)$ | $v_{2}=1\left({ }^{3} \Gamma_{5}\right)$ | $\left.\mathrm{v}_{1}=1{ }^{3} \mathrm{\Phi}_{4}\right)$ | $\mathrm{Co}^{13} \mathrm{CN}\left({ }^{3} \Phi_{4}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| B | 4200.652(29) | 4211.0379(65) | 4215.38(01) | 4237.201(81) | 4227.4183 (17) | 4199.62(35) | 4157.68 (31) |
| D | $0.000966(17)$ | $0.0020246(15)$ | $0.0016528(23)$ | $0.000599(45)$ | $0.001638(29)$ | $0.00037(17)$ | 0.00090(14) |
| H | $-5.39(44) \times 10^{-8}$ |  |  | $-2.11(11) \times 10^{-7}$ |  | -8.0(2.6) $\times 10^{-8}$ | $-5.0(2.2) \times 10^{-8}$ |
| L | $2.08(41) \times 10^{-12}$ |  |  | $1.28(10) \times 10^{-11}$ |  |  |  |
| $\mathrm{h}_{\Omega}$ | 1754.0(5.8) | 938.7(7.0) | 1065(104) | 1451(34) | 2702(56) | 1807.7(7.0) | $1780(12)$ |
| had |  |  | $0.150(50)$ | 0.049(14) | 0.085(23) |  |  |
| rms | 0.065 | 0.077 | 0.078 | 0.079 | 0.093 | 0.047 | 0.080 |

a) Errors are $3 \sigma$ and apply to last quoted place.

Table 5. Bond lengths for Transition Metal Cyanides

|  |  | $\mathrm{Im}_{\mathrm{M}}(\AA)$ | $\operatorname{rcn}(\AA)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{CoCN}^{2}$ | $\mathrm{F}_{0}(\Omega=4)$ | 1.8827(7) | $1.1313(10)$ |
|  |  |  |  |
| $\mathrm{NiCN}^{\text {b }}$ | $\mathrm{I}_{0}$ | 1.8283(6) | $1.1578(8)$ |
|  | $\mathrm{T}_{0}(\Omega=5 / 2)$ | 1.8293(1) | $1.1590(2)$ |
|  | $\mathrm{r}_{5}(\Omega=5 / 2)$ | 1.8292 | 1.1534 |
|  | $\mathrm{Im}^{(1)}(\Omega=5 / 3)$ | 1.8263(9) | 1.152(1) |
|  |  |  |  |
| CuCN ${ }^{\text {c }}$ | ${ }_{0}$ | 1.83231(7) | $1.1576(1)$ |
|  | $r_{\text {s }}$ | $1.83284(4)$ | $1.15669(3)$ |
|  | $\mathrm{r}_{\mathrm{m}}{ }^{(1)}$ | 1.8358 | 1.1573 |
|  |  |  |  |
| $\mathrm{ZnCN}{ }^{\text {d }}$ | 10 | 1.9545 | 1.1464 |
|  | $r_{\text {s }}$ | 1.9525 | 1.1434 |
|  | $\mathrm{Im}^{\text {(1) }}$ | 1.9496 | 1.1417 |

a) Calculated from $\Omega=4$ data only.
b) Reference [14]
c) Reference [11].
d) Reference [12].

## Figure Captions

Figure 1. A stick spectrum of the $J=45 \leftarrow 44$ rotational transition of $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{\mathrm{i}}\right)$ near 380 GHz is presented. Each hyperfine octet is represented by a single feature, with its approximate relative experimental intensity. The strongest line is the ground state $\Omega=4$ spin-orbit component and second most intense feature is the $\Omega=3$ spin-component, both belonging to the ground vibrational state. The remaining lines belong to the vibronic components of the bending vibrational mode and metal - carbon stretch, labeled by $\left(\mathrm{K}_{\mathrm{P}}\right)$. The first quantum of the stretch, $\mathrm{N}_{1}$ $=1\left({ }^{3} \Phi_{4}\right)$ is located approximately 100 MHz higher in frequency to the ground state line perturbed presumably by Fermi resonance. The two Renner components of the $\mathrm{v}_{2}=1$ vibronic level $\left({ }^{3} \Delta_{3}\right.$ and $\left.{ }^{3} \Gamma_{5}\right)$ are located approximately 2 and 3 GHz higher respectively in frequency. Approximately $5-6 \mathrm{GHz}$ higher in frequency/from the ground state line, two transitions arising from the $v_{2}=2$ vibronic level are found.

Figure 2. A laboratory spectrum of the $\Omega=4,3$, and 2 spin-orbit components of the $\mathrm{J}=45$ 44 rotational transition of $\operatorname{CoCN}\left(\mathrm{X}^{3} \Phi_{i}\right)$ near 378 GHz is presented. The strongest feature is the $\Omega=4$ spin component followed by the $\Omega=3$ and 2 sub-levels. Two frequency gaps of approximately 500 MHz are present in the figure. For each component, the hyperfine splitting due to the ${ }^{59} \mathrm{Co}(\mathrm{I}=7 / 2)$ nucleus is clearly resolved. The spectrum is compilation of three, 100 MHz scans, each 1 min in duration.

Figure 3. A laboratory spectrum of the $\Omega=4$ spin-orbit component of the $\mathrm{J}=48 \leftarrow 47$ rotational iransition of $\mathrm{C}^{13} \mathrm{CN}$ near 398.6 GHz . Although the intensity of the signal is weak, all
eight spin-components are clearly present in the highlighted area. The spectrum is an average of two, 100 MHz scans, each 1 min in duration.




EPAPS Table 1. Measured Rotational Transition Frequencies for Vibronic Components of $\operatorname{CoCN}\left(X^{3} \Phi_{i}\right)^{\text {a }}$

| 5 | $\mathrm{F}^{+}$ | $\leftarrow$ | J" | $\mathrm{F}^{\prime \prime}$ | $v_{2}=1\left({ }^{3} \Gamma_{5}\right)$ |  | $v_{2}=1\left({ }^{3} \Gamma_{5}\right)$ |  | $\mathrm{v}_{1}=1\left({ }^{3} \Phi_{4}\right)$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  | $\nu_{\text {obs }}$ | $\nu_{\text {obs }}$ cale | $\nu_{\text {obs }}$ | $v_{\text {obs-catc }}$ | $V_{\text {obs }}$ | $v_{\text {obs }}$ calc |
| 44 | 40.5 |  | 43 | 39.5 | 371469.333 | -0.021 | 372506.472 | -0.057 |  |  |
| 44 | 41.5 |  | 43 | 40.5 | 371465.710 | -0.107 | 372503.295 | -0.079 |  |  |
| 44 | 42.5 |  | 43 | 41.5 | 371462.050 | -0.048 | 372500.042 | -0.011 |  |  |
| 44 | 43.5 |  | 43 | 42.5 |  |  | 372496.636 | 0.068 |  |  |
| 44 | 44.5 |  | 43 | 43.5 | 371454.100 | -0.018 | 372492.824 | -0.097 |  |  |
| 44 | 45.5 |  | 43 | 44.5 | 371449.824 | -0.038 | 372489.151 | 0.038 |  |  |
| 44 | 46.5 |  | 43 | 45.5 | 371445.460 | 0.029 |  |  |  |  |
| 44 | 47.5 |  | 43 | 46.5 | 371440.855 | 0.027 |  |  |  |  |
| 45 | 41.5 |  | 44 | 40.5 | 379884.529 | -0.043 | 380946.792 | -0.005 | 377754.484 | .0.002 |
| 45 | 42.5 |  | 44 | 41.5 | 379881.044 | -0.146 | 380943.898 | 0.117 | 377751.460 | 0.024 |
| 45 | 43.5 |  | 44 | 42.5 | 379877.628 | -0.009 | 380940.570 | -0.040 | 377748.304 | 0.063 |
| 45 | 44.5 |  | 44 | 43.5 | 379873.938 | 0.022 | 380937.285 | -0.001 | 377744.884 | -0.018 |
| 45 | 45.5 |  | 44 | 44.5 | 379869.937 | -0.090 | 380933.851 | 0.040 | 377741.431 | 0.011 |
| 45 | 46.5 |  | 44 | 45.5 | 379865.919 | -0.055 | 380930.238 | 0.054 | 377737.739 | -0.058 |
| 45 | 47.5 |  | 44 | 46.5 | 379861.799 | 0.042 | 380926.356 | -0.054 | 377734.010 | -0.023 |
| 45 | 48.5 |  | 44 | 47.5 | 379857.339 | -0.039 | 380922.443 | -0.044 | 377730.133 | 0.002 |
| 46 | 42.5 |  | 45 | 41.5 |  |  | 389385.020 | 0.077 | 386133.652 | -0.005 |
| 46 | 43.5 |  | 45 | 42.5 | 388294.815 | -0.014 | 389382.094 | 0.036 | 386130.723 | -0.006 |
| 46 | 44.5 |  | 45 | 43.5 | 388291.428 | -0.006 | 389379.050 | 0.022 | 386127.647 | -0.019 |
| 46 | 45.5 |  | 45 | 44.5 | 388287.937 | 0.057 | 389375.889 | 0.035 | 386124.477 | 0.010 |
| 46 | 46.5 |  | 45 | 45.5 | 388284.226 | 0.056 | 389372.557 | 0.018 | 386121.070 | -0.066 |
| 46 | 47.5 |  | 45 | 46.5 | 388280.277 | -0.028 | 389369.033 | -0.050 | 386117.687 | 0.016 |
| 46 | 48.5 |  | 45 | 47.5 | 388276.256 | -0.031 | 389365.417 | -0.070 | 386114.117 | 0.041 |
| 46 | 49.5 |  | 45 | 48.5 | 388272.111 | -0.008 | 389361.889 | 0.135 | 386110.379 | 0.029 |
| 47 | 43.5 |  | 46 | 42.5 | 396709.856 | 0.064 | 397820.973 | 0.089 | 394511.502 | -0.013 |
| 47 | 44.5 |  | 46 | 43.5 | 396707.112 | 0.419 | 397818.078 | -0.043 | 394508.815 | 0.112 |

EPAPS Table 1. Cont'd

| ( ${ }^{3}$ - Table 1. Cont |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| J' | F' | $\leftarrow$ | $\mathrm{J}^{\prime \prime}$ | $F^{\prime \prime}$ | $\nu_{\text {obs }}$ | $\nu_{\text {obs }}$ catc | $v_{\text {obs }}$ | $\nu_{\text {obs }}$-calc | $v_{\text {obs }}$ | $v_{\text {obs*calc }}$ |
| 47 | 45.5 |  | 46 | 44.5 | 396703.499 | 0.054 | 397815.271 | 0.047 | 394505.660 | -0.103 |
| 47 | 46.5 |  | 46 | 45.5 | 396700.062 | 0.013 | 397812.090 | -0.101 | 394502.652 | -0.045 |
| 47 | 47.5 |  | 46 | 46.5 | 396696.528 | 0.022 | 397808.941 | -0.085 | 394499.515 | 0.009 |
| 47 | 48.5 |  | 46 | 47.5 | 396692.758 | -0.060 | 397805.675 | -0.054 | 394496.229 | 0.039 |
| 47 | 49.5 |  | 46 | 48.5 | 396688.974 | -0.012 | 397802.362 | 0.061 | 394492.735 | -0.017 |
| 47 | 50.5 |  | 46 | 49.5 | 396685.021 | 0.008 | 397798.728 | -0.015 | 394489.208 | 0.017 |
| 48 | 44.5 |  | 47 | 43.5 |  |  |  |  |  |  |
| 48 | 45.5 |  | 47 | 44.5 |  |  |  |  |  |  |
| 48 | 46.5 |  | 47 | 45.5 |  |  |  |  |  |  |
| 48 | 47.5 |  | 47 | 46.5 |  |  |  |  |  |  |
| 48 | 48.5 |  | 47 | 47.5 |  |  |  |  |  |  |
| 48 | 49.5 |  | 47 | 48.5 |  |  | - |  |  |  |
| 48 | 50.5 |  | 47 | 49.5 |  |  |  |  |  |  |
| 48 | 51.5 |  | 47 | 50.5 |  |  |  |  |  |  |
| 55 | 51.5 |  | 54 | 50.5 | 463934.995 | 0.066 | 465219.844 | 0.065 |  |  |
| 55 | 52.5 |  | 54 | 51.5 | 463932.620 | -0.067 | 465217.626 | -0.159 |  |  |
| 55 | 53.5 |  | 54 | 52.5 | 463930.384 | 0.031 | 465215.701 | -0.006 |  |  |
| 55 | 54.5 |  | 54 | 53.5 | 463927.865 | -0.061 | 465213.456 | -0.089 |  |  |
| 55 | 55.5 |  | 54 | 54.5 | 463925.420 | 0.012 | 465211.140 | -0.161 |  |  |
| 55 | 56.5 |  | 54 | 55.5 | 463922.831 | 0.032 | 465208.865 | -0.108 |  |  |
| 55 | 57.5 |  | 54 | 56.5 | 463920.135 | 0.034 | 465206.661 | 0.096 |  |  |
| 55 | 58.5 |  | 54 | 57.5 | 463917.413 | 0.099 . | 465204.265 | 0.190 |  |  |
| 56 | 52.5 |  | 55 | 51.5 | 472328.844 | -0.020 | 473632.596 | 0.051 |  |  |
| 56 | 53.5 |  | 55 | 52.5 | 472326.615 | -0.091 | 473630.556 | -0.070 |  |  |
| 56 | 54.5 |  | 55 | 53.5 | 472324.356 | -0.103 | 473628.575 | -0.052 |  | - |
| 56 | 55.5 |  | 55 | 54.5 | 472322.127 | 0.001 | 473626.551 | 0.002 |  |  |
| 56 | 56.5 |  | 55 | 55.5 | 472319.726 | 0.020 | 473624.473 | 0.081 |  |  |

EPAPS Table 1. Cont'd

| $v_{2}=1$ |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| J | $\mathrm{F}^{6}$ | $\leftarrow$ | $\mathrm{J}^{\prime \prime}$ | $F^{\prime \prime}$ | $v_{\text {obs }}$ | $\nu_{\text {obs }}$ calc | $v_{\text {obs }}$ | $\nu_{\text {obs-calc }}$ | $\nu_{\text {obs }}$ | $\nu_{\text {obs }}$-calc |
| 56 | 57.5 |  | 55 | 56.5 | 472317.211 | 0.011 | 473622.142 | -0.016 |  |  |
| 56 | 58.5 |  | 55 | 57.5 | 472314.729 | 0.119 | 473619.842 | -0.004 |  |  |
| 56 | 59.5 |  | 55 | 58.5 | 472311.909 | -0.026 | 473617.430 | -0.027 |  |  |
| 57 | 53.5 |  | 56 | 52.5 | 480720.793 | 0.177 | 482042.592 | 0.154 |  |  |
| 57 | 54.5 |  | 56 | 53.5 | 480718.352 | -0.185 | 482040.633 | 0.043 |  |  |
| 57 | 55.5 |  | 56 | 54.5 | 480716.241 | -0.133 | 482038.744 | 0.078 |  |  |
| 57 | 56.5 |  | 56 | 55.5 | 480714.123 | -0.006 | 482036.646 | -0.022 |  |  |
| 57 | 57.5 |  | 56 | 56.5 | 480711.862 | 0.059 | 482034.554 | -0.041 |  |  |
| 57 | 58.5 |  | 56 | 57.5 | 480709.329 | -0.065 | 482032.435 | -0.013 |  |  |
| 57 | 59.5 |  | 56 | 58.5 | 480706.717 | -0.188 | 482030.217 | -0.010 |  |  |
| 57 | 60.5 |  | 56 | 59.5 | 480704.526 | 0.189 | 482027.896 | -0.038 |  |  |
| 58 | 54.5 |  | 57 | 53.5 | 489110.342 | 0.198 |  |  |  |  |
| 58 | 55.5 |  | 57 | 54.5 | 489108.059 | -0.082 |  |  |  |  |
| 58 | 56.5 |  | 57 | 55.5 | 489106.023 | -0.035 | 490445.789 | 0.003 |  |  |
| 58 | 57.5 |  | 57 | 56.5 | 489103.893 | -0.004 | 490443.822 | -0.041 |  |  |
| 58 | 58.5 |  | 57 | 57.5 | 489101.678 | 0.020 | 490441.822 | -0.047 |  |  |
| 58 | 59.5 |  | 57 | 58.5 | 489099.338 | -0.004 | 490439.849 | 0.044 |  |  |
| 58 | 60.5 |  | 57 | 59.5 | 489097.034 | 0.084 | 490437.804 | 0.133 |  |  |
| 58 | 61.5 |  | 57 | 60.5 | 489094.433 | -0.049 | 490435.569 | 0.101 |  |  |
| 59 | 55.5 |  | 58 | 54.5 |  |  |  |  |  |  |
| 59 | 56.5 |  | 58 | 55.5 |  |  |  |  |  |  |
| 59 | 57.5 |  | 58 | 56.5 | 497493.431 | -0.039 |  |  |  |  |
| 59 | 58.5 |  | 58 | 57.5 | 497491.365 | -0.024 |  |  |  |  |
| 59 | 59.5 |  | 58 | 58.5 | 497489.273 | 0.039 |  |  |  |  |
| 59 | 60.5 |  | 58 | 59.5 | 497487.029 | 0.023 | 498844.058 | -0.141 |  |  |
| 59 | 61.5 |  | 58 | 60.5 | 497484.748 | 0.043 | 498842.069 | -0.079 |  |  |
| 59 | 62.5 |  | 58 | 61.5 | 497482.211 | -0.121 | 498840.083 | 0.053 |  |  |

a) $\operatorname{In~} \mathrm{MHz}$.


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[^2]:    2 The complete data sel may the purchased from the Depository of Unpublished Data. Document Delivery. CiSTl. Aialional Researth Council Canads. Ontawa. ON KIA OS2. Canada. For information on ordering electronically use the following web address: bup://\&ww:nre.ca cishii imm/unpub_e.shimil

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[^8]:    In MHz: errors are 3 ar and apply to the lase quoted decimal places.
    
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[^11]:    a) $\ln \mathrm{MHz}$; for the $v=1$ daia set, please contact the authors.

