# High-resolution visible laser spectroscopy of the $\tilde{B}^{2} B_{1}-\tilde{X}^{2} A_{1}$ transition of $\mathrm{CaNH}_{2}$ 

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#### Abstract

The $0_{0}^{0} \widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$ band of $\mathrm{CaNH}_{2}$ has been recorded at high resolution with a laser ablation molecular beam spectrometer. This $\widetilde{B}^{2} B_{1}$ state is the last of the low-lying electronic states of $\mathrm{CaNH}_{2}$ to be characterized. The pure precession model, which has previously been used to describe the spin-rotation interactions in this family of molecules was used to interpret and correctly assign the spectrum. The detailed analysis of the high resolution spectrum and energy level structure of the $\widetilde{B}{ }^{2} B_{1}$ state is presented. © 1998 American Institute of Physics. [S0021-9606(98)00121-4]


## I. INTRODUCTION

The analysis of the $\widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$ transition completes the high resolution spectroscopic study of the low-lying electronic states of $\mathrm{CaNH}_{2}$. ${ }^{1,2}$ The monovalent derivatives of the alkaline-earth molecules ( $\mathrm{MX}, \mathrm{M}=\mathrm{Mg}, \mathrm{Ca}, \mathrm{Sr}, \mathrm{Ba}$ ) have an electronic structure that can be described by a one-electron hydrogenic picture. This rather unique property is partly responsible for the many research papers devoted to this family of molecules. ${ }^{3,4}$ The study of the metal-ligand bond is an important aspect of modern chemistry and the alkaline-earth molecules have given researchers ${ }^{3,4}$ ample opportunity to study the metal-halide, metal-oxygen, metal-carbon, metal-sulfur, and metal-nitrogen bonds. Molecules with metal-oxygen bonds are important in atmospheric and combustion chemistry, ${ }^{5,6}$ while metal-carbon and metalnitrogen bonds are found in biological systems, ${ }^{3,4}$ such as the active sites of enzymes, while metal-sulfur systems have applications in industrial chemical processes.

While the spectroscopy of the low-lying electronic states of alkaline-earth molecules is fairly well understood, the reactions which generate them are not. Studies to date have been concerned with the reaction of an alkaline-earth atom with water or alcohols. In the two mechanisms that have been proposed, the rate limiting step is the insertion of the metal atom into the $\mathrm{H}-\mathrm{OR}$ bond. This step forms an intermediate species such as $\mathrm{H}-\mathrm{Ba}-\mathrm{OR}\left(\mathrm{R}=\mathrm{H}, \mathrm{CH}_{3}, \mathrm{C}_{2} \mathrm{H}_{5} \cdots\right)$. Different products can be generated from this reaction where $\mathrm{BaH}, \mathrm{BaO}$ or BaOR have all been observed under widely different experimental conditions. The dynamics of a few reactions of $\mathrm{H}_{2} \mathrm{O}$ and ROH with alkaline earths have been studied in detail and they show that the reactivity is strongly dependent on the electronic state of the alkaline-earth atom ${ }^{7-9}$ and also on the size of the reacting species. ${ }^{10-12}$ For example, ground state Ba atoms react with $\mathrm{H}_{2} \mathrm{O}$ to give predominantly the BaO product while ${ }^{1} D \mathrm{Ba}$ atoms favor the

[^0]BaOH product, even though BaO is favored on energetic grounds. ${ }^{13}$ There is a great need for experimental work on the kinetics and dynamics of the reactions before a good understanding of the reaction mechanisms can be achieved.

The spectroscopy of the high-lying or Rydberg electronic states of the alkaline-earth molecules has also not been extensively studied. Rydberg states of CaF and more recently $\mathrm{CaOH}^{14,15}$ and $\mathrm{CaOD}^{15}$ have been studied mainly by optical-optical double resonance (OODR) techniques. The theoretical calculations of Ortiz ${ }^{16}$ are in good agreement with the experimentally observed electronic states. The work of Pereira and Levy, OODR in a molecular beam detected by R2PI, has shown that one excited electronic state ( $\widetilde{F}^{\prime \prime}{ }^{2} \Pi^{\prime \prime}$ ) has a bent geometry while the next higher-lying electronic state, $\widetilde{G}^{2} \Pi$, is linear. ${ }^{15}$ It is well known that the bonding in the low-lying electronic states is predominantly ionic leading to linear geometries. Further theoretical and experimental work needs to be done to determine what dictates the geometry in the excited state.

We have previously reported the high resolution analysis of the $\widetilde{C}-\widetilde{X}$ system of $\mathrm{CaNH}_{2}{ }^{2}$ and this work was preceded by a high resolution analysis of the $\tilde{A}-\widetilde{X}$ system by Marr et al. ${ }^{1}$ Other work on $\mathrm{CaNH}_{2}$ has included low resolution studies in a Broida oven ${ }^{17,18}$ and a moderate resolution study using a laser ablation molecular beam spectrometer. ${ }^{19}$ In this paper we discuss the spectroscopy of the $\widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$ system and the details of the pure precession model that helped us to correctly assign the spectrum.

## II. EXPERIMENT

The experimental apparatus consists of a source compartment containing a Smalley-type laser ablation source and a second detection chamber. The experimental arrangement has been described in previous publications. ${ }^{2,20}$ Briefly, a 10 ns pulse of 532 nm radiation from a Nd:YAG (Continuum: Surelite) laser is gently focused onto a rotating calcium rod. The laser-produced metal plasma reacts with ammonia gas coexpanded with an inert carrier ( $5 \% \mathrm{NH}_{3}$ in Ar ) which is held at $50-60$ psi behind a pulsed valve $(10 \mathrm{~Hz})$. The $\mathrm{CaNH}_{2}$


FIG. 1. Some of the assigned branches of the $0-1$ subband in the $0_{0}^{0} \widetilde{B}^{2} B_{2}-\tilde{X}^{2} A_{1}$ transition of $\mathrm{CaNH}_{2}$. This spectrum corresponds to a ${ }^{2} \Sigma$-case (b) ${ }^{2} \Pi$ electronic transition of a linear molecule. The $Q$-branch lines are not labeled for clarity.
molecules are subsequently probed by the output of a singlemode ( 1 MHz ) CW ring dye laser (Coherent 699-29) about 15 cm downstream from the nozzle. Detection of the $\mathrm{CaNH}_{2}$ species was carried out by averaging the laser-induced fluorescence (LIF) signal in the time window between 175-205 $\mu \mathrm{s}$ after the laser ablation pulse. This is the time required for the $\mathrm{CaNH}_{2}$ molecules to travel the 15 cm to the detection region. The LIF passes through a $630 \pm 5 \mathrm{~nm}$ bandpass filter and is collimated with a 1.5 in . lens and focused onto a photomultiplier tube with a 7 in . lens. A 5 mm aperture is used to limit the field of view and it reduces the Doppler linewidth to approximately $150-200 \mathrm{MHz}$. The laser was calibrated by splitting off a small fraction of the beam to record the LIF spectrum of $\mathrm{I}_{2}$ in a static gas cell. ${ }^{21,22}$

## III. RESULTS AND ANALYSIS

The $\tilde{A}-\tilde{X}$ and $\tilde{C}-\tilde{X}$ band systems of $\mathrm{CaNH}_{2}$ have previously been recorded and analyzed at high resolution. A detailed analysis of $\widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$ transition, which occurs near 629 nm , has not been carried out. However, the low resolution laser excitation spectrum has been studied, ini-


FIG. 2. The assigned branches of the $1-0$ subband in the $0_{0}^{0} \widetilde{B}^{2} B_{2}-\widetilde{X}^{2} A_{1}$ transition of $\mathrm{CaNH}_{2}$. Note the intermediate case (a)-(b) behavior in the excited state (see the text for details).


FIG. 3. The $2-1$ subband of the $\widetilde{B}^{2} B_{2}-\widetilde{X}^{2} A_{1}$ electronic transition of $\mathrm{CaNH}_{2}$. The origins and band gap are evident for the $F_{1}$ and $F_{2}$ spin components.
tially in a high temperature source (Broida oven) ${ }^{18}$ and later with a laser ablation/molecular beam spectrometer ${ }^{19}$ using a pulsed dye laser as a probe.
$\mathrm{CaNH}_{2}$ is a planar $\left(C_{2 v}\right)$, near prolate asymmetric top molecule, and thus the electronic transitions can be classified as parallel (a-type) or perpendicular (b- or c-type). The $\widetilde{B}-\widetilde{X}$ transition corresponds to the promotion of an electron from a ground state metal-centered $s$-type orbital to a predominantly metal-centered $p_{x}$-type orbital (see Figs. 1 and 2 of Ref. 2), where the $p_{x}$ orbital is perpendicular to the plane of the molecule. A $p_{x} \leftarrow s$ electronic transition is therefore a c-type perpendicular transition. The spectrum will consist of subbands separated by approximately $2 A$ ( $A$ is the largest of the three rotation constants), where each subband originates


FIG. 4. The energy level diagram for the $1-0$ subband of the $\widetilde{B}^{2} B_{2}-\tilde{X}^{2} A_{1}$ transition.


FIG. 5. The energy level diagram for the $0-1$ subband of the $\widetilde{B}^{2} B_{2}-\widetilde{X}^{2} A_{1}$ transition.


FIG. 6. The energy level diagram for the $2-1$ subband of the $\widetilde{B}^{2} B_{2}-\tilde{X}^{2} A_{1}$ transition.


FIG. 7. The energy level diagram for the $1-1$ subband of the $\widetilde{C}^{2} A_{1}-\widetilde{X}^{2} A_{1}$ transition using the labeling scheme adopted in this paper, see the text for details.
from a different $K_{a}^{\prime \prime}$ value of the molecule. The selection rule for a c-type transition is, $\Delta K_{a}= \pm 1\left(\Delta K_{c}=0\right)$ giving rise to $\left(K_{a}^{\prime} \leftarrow K_{a}^{\prime \prime}\right) 0-1,1-0$, and 2-1, etc., subbands. As was found with the $\widetilde{C}-\widetilde{X}$ transition of $\mathrm{CaNH}_{2}$, the free jet expansion cools all of the ortho (odd $K_{a}^{\prime \prime}$ ) rotational levels into $K_{a}^{\prime \prime}=1$ and the para $\left(\right.$ even $\left.K_{a}^{\prime \prime}\right)$ levels into $K_{a}^{\prime \prime}=0$. But, unlike the parallel $\widetilde{C}-\tilde{X}$ transition, where all of the subbands are overlapped due to the $\Delta K_{a}=0$ selection rule, the subbands of the $\widetilde{B}-\widetilde{X}$ transition are separated by approximately $26 \mathrm{~cm}^{-1}$. Therefore, the high resolution analysis of this band system is somewhat simpler than the spectrum of the $\widetilde{C}-\tilde{X}$ transition.

The appearance of the high resolution spectrum can be related to analogous transitions of a diatomic or linear molecule. The $0-1$ (Fig. 1) subband has the appearance of a ${ }^{2} \Sigma-\left[\right.$ Hund's case (b)] ${ }^{2} \Pi$ transition while the $1-0$ (Fig. 2)

TABLE I. The spectroscopic constants for $\mathrm{CaNH}_{2}$ in $\mathrm{cm}^{-1}$.

|  | $\widetilde{X}^{2} A_{1}$ | $\widetilde{B}^{2} B_{1}$ |
| :--- | :---: | :---: |
| $T_{0-0}$ | 0 |  |
| $A$ | $13.057452(598)$ | $15885.281096(869)$ |
| $\frac{1}{2}(B+C)$ | $0.2966572(126)$ | $14.36492(132)$ |
| $\frac{1}{4}(B-C)$ | $1.89167(436) \times 10^{-3}$ | $0.3017199(194)$ |
| $\epsilon_{a a}$ | 0 | $3.6947(536) \times 10^{-3}$ |
| $\frac{1}{2}\left(\epsilon_{b b}+\epsilon_{c c}\right)$ | $8.525(601) \times 10^{-4}$ | $-7.54163(157)$ |
| $\frac{1}{4}\left(\epsilon_{b b}-\epsilon_{c c}\right)$ | 0 |  |
| $\Delta_{K}$ | - | $2.05316(992) \times 10^{-2}$ |
| $\Delta_{N}$ | - | $8.321(161) \times 10^{-2}$ |
| $\delta_{K}$ | - | $-4.0843(275) \times 10^{-2}$ |
| $\Delta_{K}^{S}$ | - | $-4.69(103) \times 10^{-7}$ |
| $\Delta_{K N}^{S}$ | - | $2.0053(462) \times 10^{-3}$ |
| $\Delta_{N K}^{S}$ | - | $-1.632(132) \times 10^{-2}$ |

TABLE II. Line positions of the $\widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$ of $\mathrm{CaNH}_{2}\left(\mathrm{~cm}^{-1}\right)$.


TABLE II. (Continued.)


TABLE II. (Continued.)

| $J^{\prime \prime}$ | $\begin{aligned} & \text { Observed } \\ & { }^{P} P_{11} \end{aligned}$ | $\begin{array}{r} \Delta \times 10^{-5} \\ 0-1 \end{array}$ | $J^{\prime \prime}$ | Observed ${ }^{Q} Q_{22}$ | $\Delta \times 10^{-5}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2.5 | 15941.10501 | -15 | 4.5 | 15940.15880 | -517 |
| 3.5 | 15942.09570 | 131 | 5.5 | 15940.61245 | 102 |
| 4.5 | 15943.10640 | -61 | 6.5 | 15941.08433 | 215 |
| 5.5 | 15944.14712 | 414 | 7.5 | 15941.56978 | -640 |
| 6.5 | 15945.20563 | 339 |  |  |  |
| 7.5 | 15946.28860 | 386 |  | ${ }^{R} Q_{21}^{(N)}$ |  |
| 8.5 | 15947.39381 | 341 | 2.5 | 15922.00601 | -167 |
|  |  |  | 3.5 | 15922.31147 | -560 |
|  | ${ }^{Q} P_{21}^{(N)}$ |  | 4.5 | 15922.63751 | 694 |
| 3.5 | 15920.24319 | 462 | 5.5 | 15922.95297 | 496 |
| 4.5 | 15919.95966 | 121 | 6.5 | 15923.27004 | 86 |
| 5.5 | 15919.68280 | 36 | 7.5 | 15923.59448 | 65 |
| 6.5 | 15919.40928 | -108 | 8.5 | 15923.92481 | 312 |
| 7.5 | 15919.13909 | -292 | 9.5 | 15924.25111 | -134 |
| 8.5 | 15918.87891 | 176 | 10.5 | 15924.58809 | 232 |
| 9.5 | 15918.61651 | 100 | 11.5 | 15924.92451 | 321 |
|  | ${ }^{s} R_{21}^{(N)}$ |  |  | ${ }^{R} Q_{21}^{(N-1)}$ |  |
| 1.5 | 15923.18781 | 51 | 2.5 | 15921.99108 | 610 |
| 2.5 | 15924.08510 | - 108 | 3.5 | 15922.27322 | 154 |
| 3.5 | 15924.98683 | -237 | 4.5 | 15922.55290 | -203 |
| 4.5 | 15925.89635 | 20 | 5.5 | 15922.83195 | -260 |
| 5.5 | 15926.80142 | -541 | 6.5 | 1592310617 | -416 |
| 6.5 | 15927.71427 | -673 | 7.5 | 15923.38369 | 167 |
| 7.5 | 15928.63491 | -345 | 8.5 | 15923.64981 | 44 |
| 8.5 | 15929.56222 | 360 | 9.5 | 15923.91012 | - 193 |
| 9.5 | 15930.47952 | - 192 | 10.5 | 15924.17439 | 466 |
|  |  |  | 11.5 | 15924.42437 | 232 |
|  | $Q_{P} P_{21}^{(N-1)}$ |  | 12.5 | 15924.67098 | 237 |
| 3.5 | 15920.19983 | 665 | 13.5 | 15924.91588 | 690 |
| 4.5 | 15919.88294 | 14 | 14.5 | 15925.13836 | -436 |
| 5.5 | 15919.56939 | 42 |  |  |  |
| 6.5 | 15919.25139 | -12 |  | ${ }^{S} R_{21}^{(N-1)}$ |  |
| 7.5 | 15918.93228 | 207 | 2.5 | 15924.06286 | -63 |
| 8.5 | 15918.60650 | 167 | 3.5 | 15924.94236 | - 145 |
| 9.5 | 15918.28294 | 783 | 4.5 | 15925.81741 | -310 |
|  |  |  | 5.5 | 15926.68801 | -536 |
|  |  |  | 6.5 | 15927.55750 | -464 |
|  |  |  | 7.5 | 15928.42588 | -68 |
|  |  |  | 8.5 | 15929.28425 | -205 |
|  |  |  | 9.5 | 15930.14596 | 491 |

and $2-1$ (Fig. 3) subbands appear like case (a) ${ }^{2} \Pi\left({ }^{2} \Delta\right)-{ }^{2} \Sigma$ (case (b) ${ }^{2} \Pi$ ) transitions. This is because the spin-rotation constant, $\boldsymbol{\epsilon}_{a a}$, in $\mathrm{CaNH}_{2}$ has a similar effect as the spinorbit constant ( $A^{\mathrm{SO}}$ ) of a hypothetical linear molecule. The rotational energy levels of a near prolate doublet asymmetric top are approximately given by

$$
\begin{align*}
E\left(N, K_{a}\right)= & A K_{a}^{2} \pm \frac{1}{2} \epsilon_{a a} K_{a}+\frac{1}{2}(B+C)\left[N(N+1)-K_{a}^{2}\right] \\
& +\cdots, \tag{1}
\end{align*}
$$

where $A, B, C$ are the rotational constants, and $K_{a}$ and $N$ are angular momentum quantum quantum numbers. Thus for a subband with $K_{a}^{\prime}=0\left(0-1\right.$ subband) in the $\widetilde{B}^{2} B_{1}$ state, the excited state energy levels will approximate a ${ }^{2} \Sigma$ state of a linear molecule. The value of $\epsilon_{a a}$ in the ground state is small because the $\tilde{X}$ state originates from an $s$ orbital which does
not have any spin-orbit coupling. The $K_{a}^{\prime \prime}=1$ levels behave as a Hund's case (b) ${ }^{2} \Pi$ state and the spectrum appears like $a^{2} \Sigma$-case (b) ${ }^{2} \Pi$ transition.

For the $1-0$ subband, the excited state is like an intermediate Hund's case (a)-case (b) ${ }^{2} \Pi$ state. This is because the term, $\left|\epsilon_{a a} /(B+C) J\right| \leqslant 1 \quad\left(\epsilon_{a a}^{\prime} \simeq-7.5 \mathrm{~cm}^{-1}\right)$ for low $J$ values (i.e., $J \leqslant 15$ ). The $\widetilde{A}$ and $\widetilde{B}$ states of $\mathrm{CaNH}_{2}$ differ from the corresponding states of $\mathrm{SrNH}_{2}$, where $\left|\epsilon_{a a}\right|$ $\simeq 30 \mathrm{~cm}^{-1}$. The splitting of the $F_{1}$ and $F_{2}$ spin components in the excited electronic state is approximately given by, $\epsilon_{a a} K_{a}$, so the term $\left|\epsilon_{a a} /(B+C) J\right| \geqslant 1$, even for low $J(\leqslant 20)$ in $\mathrm{SrNH}_{2}$. Thus the $K_{a} \geqslant 1$ levels will approximate case (a) behavior in $\mathrm{SrNH}_{2}$ because of the large value of $\epsilon_{a a}$ in the $\tilde{A}$ and $\widetilde{B}$ states. The transition from pure case (a) behavior to intermediate case (a)-(b) behavior begins at high rotational angular momentum ( $J \simeq 50$ ). Some spin uncoupling was observed in the $\widetilde{A}-\tilde{X}$ and $\widetilde{B}-\widetilde{X}$ transitions of
$\mathrm{SrNH}_{2}$, since high $J$ rotational levels were populated in the Broida oven source. ${ }^{23}$ High $J$ rotational transitions were not observed in the cold spectrum of $\mathrm{CaNH}_{2}$ recorded in this work.

The difference between case (a) and intermediate case (a)-(b) behavior can clearly be seen by comparing the spectra of the $1-0$ (Fig. 2) and $2-1$ (Fig. 3) subbands. The $2-1$ subband corresponds to a case (a) ${ }^{2} \Delta$-case (b) ${ }^{2} \Pi$ transition of a linear molecule. The separation between $F_{2}$ and $F_{1}$ spin-rotation components in the excited state is roughly $17 \mathrm{~cm}^{-1} \quad\left(\left|\epsilon_{a a} K_{a}\right|=15.1 \mathrm{~cm}^{-1}\right)$, while the corresponding splitting in the $1-0$ band $\left(\nu\left({ }^{Q} Q_{22}\right)-\nu\left({ }^{Q} Q_{11}\right)\right)$ is $7.1 \mathrm{~cm}^{-1}$. A clear separation of the band origins of the $F_{1}$ and $F_{2}$ components is quite evident in the spectrum of the $2-1$ subband but is not clearly observed in the $1-0$ subband.

The fine structure of the $K_{a}=0$ rotational levels arises from spin-rotation interactions, where the splittings are proportional to $\frac{1}{2}\left(\epsilon_{b b}+\epsilon_{c c}\right)$. These levels are labelled $F_{1}$ and $F_{2}$ according to the total angular momentum $J\left(=N \pm \frac{1}{2},+\right.$ for $F_{1}$, - for $F_{2}$ ). In rotational levels with $K_{a} \neq 0$, the splitting of the $F_{1}$ and $F_{2}$ components are equivalent to a 'spinorbit'" splitting which is proportional to $\epsilon_{a a} K_{a}$. This is because the spin-rotation interactions are dominated by second order spin-orbit effects rather than first order coupling between electron spin and nuclear rotation. The second order nature of the spin-rotation interaction allows one to derive simple formulas (pure precession model, ${ }^{2}$ Coriolis interaction ${ }^{19}$ ) for the spin-rotation parameters. The small splitting within each component is due to slight asymmetry in the molecule.

The energy level diagram for a $1-0$ subband is given in Fig. 4, the transitions are labeled according to the recommendations of Marr et al., ${ }^{1}{ }^{\Delta N} \Delta J_{F_{i}^{\prime} F_{i}^{\prime \prime}}$. There are a total of 12 allowed branches in the $0-1$ and $1-0$ subbands and 8 were observed for the $0-1$ subband while 11 were observed for the $1-0$ subband. In the $2-1$ subband 14 of the 24 possible branches were observed. Energy level diagrams for the $0-1$, $1-0$, and $2-1$ subbands are depicted in Figs. 4-6. The labeling of the $F_{1}$ and $F_{2}$ components in a case (a) electronic state of an asymmetric top molecule can lead to some confusion. One can choose $F_{1}$ and $F_{2}$ according to the sign of $\epsilon_{a a}\left[\epsilon_{a a}>0\right.$ regular case (a), $\epsilon_{a a}<0$ inverted case (a)], or, the conventional spectroscopic method based on a Hund's case (a)-case (b) correlation diagram between $N$ and $J$ which leads to the identification of the $F_{1}$ and $F_{2}$ spin labels. ${ }^{24}$ In the paper by Marr et al., they chose $F_{1}$ and $F_{2}$ based on the sign of $\epsilon_{a a}$, we, however, choose the conventional scheme. The choice of the labeling scheme, however, does not effect the molecular constants or the $J$ assignment. For example, fitting the data of Marr et al. using our nonlinear least squares program gave identical constants to those in the published literature. ${ }^{1}$ The differences arise in the label of each rotational level $\left(N_{K a K c}\right)$ and the spin labels, $F_{1}$ and $F_{2}$. Using the notation adopted here, the $F_{1}$ and $F_{2}$ labels for the assigned branches of the $1-0$ and $2-1$ subbands in the $\widetilde{A}^{2} B_{2}-\widetilde{X}^{2} A_{1}$ transition should be interchanged and the $N$ (and $K_{c}$ ) quantum number label should be increased by 1 for the $F_{1}$ component and reduced by 1 for $F_{2}$, For example, the
${ }^{P} P_{22}^{N}$ branch becomes ${ }^{O} P_{12}^{N}$, since the rotational transitions are relabeled, $\left(F_{1}\right) 2_{21} \leftarrow\left(F_{2}\right) 4_{14}$, from $\left(F_{2}\right) 3_{22} \leftarrow\left(F_{2}\right) 4_{14}$ in Fig. 5 of Ref.1. In the paper of the $\widetilde{C}-\widetilde{X}$ band system of $\mathrm{CaNH}_{2},{ }^{2}$ we had labeled the rotational levels of the excited state in the $1-1$ subband using the scheme of Marr et al. For consistency we reproduce the energy level diagram using the scheme adopted in this paper (see Fig. 7). The $0-0$ energy level diagram depicted in Fig. 3 of Ref. 2 does not change since $K_{a}=0$ levels approximate a ${ }^{2} \Sigma$ states of a diatomic (linear) molecules.

The assignment of the $\widetilde{B}-\tilde{X}$ spectrum was carried out in a using a color Loomis-Wood program ${ }^{25}$ to sort the branches, and ground state combination differences were calculated with the constants of Marr et al. There were, however, problems in fitting the assigned lines. There was difficulty in simultaneously fitting all the branches with the inclusion of the highest $J$ lines. It was reasoned that there were perturbations in the $\widetilde{B}$ state similar to those found in the $\widetilde{B}$ state of $\mathrm{SrNH}_{2} \cdot{ }^{23}$ Here a Coriolis coupling between one quanta in the $\nu_{3} \mathrm{Sr}-\mathrm{N}$ stretch ( $a_{1}$ symmetry) of the $\widetilde{A}^{2} B_{2}$ state was found to interact with $v=0$ of the $\widetilde{B}{ }^{2} B_{1}$ state. Another possibility for a Coriolis interaction is between $\nu_{6}$ (NH bend $b_{2}$ symmetry) of the $\widetilde{A}^{2} B_{2}$ state with the $\widetilde{B}^{2} B_{1}$ state. The estimated location of the energy levels of the excited stretching and bending modes in the $\widetilde{A}^{2} B_{2}$ state were found to be $\sim 50 \mathrm{~cm}^{-1}$ away (to the blue and red, respectively) from $v=0$ of the energy levels of the $\widetilde{B}{ }^{2} B_{1}$ state in $\mathrm{CaNH}_{2}$. This eliminated the possibility of a local Coriolis interaction causing the problems in fitting the line positions of the $\widetilde{B}^{2} B_{1}-\widetilde{X}^{2} A_{1}$ transition. It was found that adding higher order (quartic) centrifugal distortion constants to the fit, both rotational ${ }^{26,27}$ and spin-rotational, ${ }^{28}$ alleviated the difficulties associated with fitting all the branches of each subband simultaneously. Perhaps these high order constants take into account the interactions with distant vibronic levels of the $\tilde{A}$ state.

The molecular constants for the $\widetilde{B}^{2} B_{1}$ and $\widetilde{X}^{2} A_{1}$ states are reported in Table I. These constants are obtained from fitting the data of all three low-lying electronic transitions $\left(\widetilde{A}^{2} B_{2}-\widetilde{X}^{2} A_{1},{ }_{B}{ }^{2} B_{1}-\widetilde{X}^{2} A_{1}, \widetilde{C}_{\sim}^{2} A_{1}-\widetilde{X}^{2} A_{1}{ }^{2}\right.$ ). A version of this table was published in the $\widetilde{C}-\tilde{X}$ paper, but since then we have investigated the spin-rotation parameters more carefully. In the pure precession model, the spin-rotation parameters can be predicted using a simple formula, for example, the interacting pair of states due to rotation about the $b$ axis ( $\widetilde{B}$ and $\widetilde{C}$ states), gives the following formula for the second order correction to $\epsilon_{b b}:^{2}$

$$
\begin{equation*}
\epsilon_{b b}^{(2)}= \pm \frac{2 l(l+1) B A^{\mathrm{so}}}{E_{\tilde{C}}-E_{\tilde{B}}} \tag{2}
\end{equation*}
$$

where the top sign refers to the lower lying electronic state and $l=1$ for $p$ orbitals. This model also predicts that $\epsilon_{c c}^{(2)}=0$ for the $\widetilde{B}^{2} B_{1}$ state. In the previous paper, the observed value of the spin-rotation constants derived from a global fit of the dataset are $\epsilon_{b b}^{\mathrm{obs}}=0.00351 \mathrm{~cm}^{-1}$ and $\epsilon_{c c}^{\mathrm{obs}}=0.0389 \mathrm{~cm}^{-1}$ while the pure precession model predicted the following values: $\epsilon_{b b}^{(2)}=0.0539 \mathrm{~cm}^{-1}$ and $\epsilon_{c c}^{(2)}=0 \mathrm{~cm}^{-1}$. At the time of
publication we believed the large discrepancy between the observed values and the predicted values were due to the failure of the pure precession model which assumed that the unpaired electron belongs in an pure $p$-type orbital. It was suggested to us ${ }^{29}$ that perhaps the values of $\epsilon_{b b}$ and $\epsilon_{c c}$ could be interchanged to improve the agreement with the predictions of the pure precession model. In terms of fitted constants, this would mean that the observed value of the term, $\frac{1}{4}\left(\epsilon_{b b}-\epsilon_{c c}\right)$, would have to change sign in the $\widetilde{B}^{2} B_{1}$ state. This term is a correction term due to the slight asymmetry (indicated by $\gamma=1$ or $\gamma=0$ ) of the molecule in a particular rotational level ( $N_{K_{a} K_{c}}$ ) with $K_{a} \neq 0$. By simply changing the sign of this term and leaving all other constants unchanged, it was found that the residuals of the fit in the $1-0$ subband were more than an order of magnitude larger than the uncertainty of their line positions. This is because the asymmetry splitting in $K_{a}=1$ is significantly larger than in $K_{a}=2$. We then interchanged the assignment of the asymmetry components in the $1-0$ subband and refit the data. This reassignment reduced the residuals down to the experimental uncertainty of the line positions and the sign of the term, $\frac{1}{4}\left(\epsilon_{b b}\right.$ $-\epsilon_{c c}$ ) became positive. From these fits we find the values for the spin-rotation parameters are now $\epsilon_{b b}^{\mathrm{obs}}=0.0372 \mathrm{~cm}^{-1}$ and $\epsilon_{c c}^{\mathrm{obs}}=0.00389 \mathrm{~cm}^{-1}$, which is in much better agreement with the pure precession model. This was further confirmed by finding the first lines in the spectrum of the $1-0$ subband. The first line of the ${ }^{P} P_{11}(1.5)$ branch is predicted to occur at $15903.2289 \mathrm{~cm}^{-1}$. The observed line was found at $15903.2224 \mathrm{~cm}^{-1}$ confirming the correctness of the new assignment of the $1-0$ subband. We have also confirmed the assignment of the asymmetry components of the $\widetilde{C}-\widetilde{X}$ transition. In this case, the prediction for the first line of the ${ }^{P} P_{11}^{1}(1.5)$ is $17374.5830 \mathrm{~cm}^{-1}$ which should be compared to the observed position at $17374.5765 \mathrm{~cm}^{-1}$. The usefulness of the simple pure precession model is illustrated by this example.

## IV. CONCLUSION

Laser ablation sources coupled with supersonic expansions have provided researchers with a powerful technique for the analysis of the electronic spectra of polyatomic molecules. These spectra could not be recorded easily in any other way regardless of the resolution of the probe laser. High temperature sources such as the Broida oven was the most widely used method to generate the alkaline earth containing diatomic and polyatomic molecules. This method is not suitable for the rotational analysis of larger polyatomic molecules. It is only from high resolution studies that we can elucidate the details of structure and bonding in molecular systems.

The pure precession model has been used to describe the spin-rotation interactions in the alkaline-earth family of molecules. ${ }^{3,4}$ We have presented a case where the model can be used to help correctly assign the spectrum of an open shell asymmetric molecule. The utility of this model for other polyatomic molecules with more complex spectra should be of considerable interest.

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