A high-resolution analysis of the $\tilde{C}^2A_1^–\tilde{X}^2A_1$ transition of CaNH$_2$: Pure precession in polyatomic molecules

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The high resolution spectrum of the 0$_0^0$ vibronic band of the $\tilde{C}^2A_1^–\tilde{X}^2A_1$ transition of CaNH$_2$ was recorded with a laser ablation/supersonic molecular beam spectrometer. Approximately 140 lines of the $K_a^0=0$ and $K_a^0=1$ sub–bands were measured and combined with the previous $\tilde{A}^2B_2^–\tilde{X}^2A_1$ and $\tilde{B}^2B_1^–\tilde{X}^2A_1$ results. A global fit of the data was carried out and the effective spectroscopic constants for the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$ states are reported. A complete set of spin–rotation constants ($\epsilon_{\alpha\alpha}$'s) are now available for the $\tilde{A}^2B_2$, $\tilde{B}^2B_1$ and $\tilde{C}^2A_1$ states. The unpaired electron in these three excited states can be considered to be located in three $p$–orbitals centered on the metal atom. The simple pure precession model provides estimates for the 9 spin–rotation parameters in the $\tilde{A}$, $\tilde{B}$, and $\tilde{C}$ states. © 1997 American Institute of Physics.

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I. INTRODUCTION

There has been a recent resurgence of interest in spectroscopic studies of the alkaline earth–containing polyatomic molecules. The molecules CaOH,$^1$,$^2$ SrOH,$^3$ and CaCCH (Refs. 4–6) have been studied using a high temperature source called a Broida oven. $^7$ Much of the new work, however, has been carried out with the supersonic molecular beam technique which has allowed the study of large polyatomic molecules at high resolution. The low rotational (5–20 K) and vibrational (–300 K) temperatures allows detailed information such as the fine structure, hyperfine structure, asymmetry splittings and dipole moments to be extracted from the spectra. The most novel and interesting examples from this family of molecules are the alkaline earth half-sandwich molecules,$^8$ which were studied in great detail by the Miller group.$^9$–$^{14}$ The high resolution experiments illustrate the wealth of spectroscopic information that can be obtained. Related studies include recent experiments on the singly charged alkaline earth–containing complexes such as Ca$^+$ (H$_2$O),$^{15}$ Mg$^+$ (H$_2$O) (Ref. 16) and their deuterated analogs. The electronic transitions of these molecules occur at higher energy ($\geq$21 500 cm$^{-1}$) compared to those of the isoelectronic CaNH$_2$ and MgNH$_2$ molecules.

The alkaline earth–containing polyatomic molecules were first studied by Harris and co-workers$^3$ and then further extended by Bernath and co-workers.$^{18}$–$^{24}$ These researchers used a Broida–type oven, which is a relatively high temperature (400–500 K) molecular source that is convenient for Doppler–limited studies.$^{25}$ For a non–linear polyatomic molecule, the information available from these spectra is limited due to congestion by many overlapping lines. Thus, only a partial vibronic analysis was possible for most of the non–linear polyatomic molecules.$^8$–$^{26}$–$^{30}$

The Broida oven illustrated the close connection between the spectra of the polyatomic alkaline earth derivatives and the well understood spectra of the alkaline earth monohalide molecules. The basic properties of the monohalides (e.g. electronic origins, spin–orbit splittings, lifetimes, dipole moments, etc.,...) are well described by the ligand field model proposed by Rice, Martin and Field.$^{31}$ This model treats the ligand (X$^−$) as a point charge that influences the non-bonding valence electron on the metal (M$^+$) ion. For example, the Ca$^+$ ion is perturbed by the electrostatic field of the fluoride anion (F$^−$), with the Ca$^+$ ion modelled as a closed shell Ca$^{2+}$ core with a single valence electron. The approach of the F$^−$ ligand destroys the spherical symmetry of the 4s atomic orbital and gives rise to the X $^2S^+$ state of the CaF molecule (Fig. 1).

Electronic excitation can be considered as transitions of this 4s electron to a predominately 4p orbital “belonging” to the Ca$^+$ ion. The doubly degenerate 4$p\pi$ orbitals give rise to the A $^2Π$ state, while the 4$p\sigma$ orbital results in the B $^2Σ^+$ excited state of the CaF molecule. Orbital mixing calculations were performed for CaF by Rice et al. showed that the X state has $\sim$80% 4s$\pi$ character and $\sim$20% 4p$\sigma$, while the A $^2Π$ state was a 70:30 mixture of 4p$\pi$ and 3d$\pi$ and the B $^2Σ^+$ state is approximately a 50:50 mixture of 4p$\sigma$ and 3d$\sigma$.

Further extension of the ligand field model is made by substituting the fluoride ligand with various polyatomic ligands such as OH$^−$,$^{32}$ CCH$^−$, SH$^−$, NH$_2^−$, C$_3$H$_5^−$. This replacement lowers the symmetry of the molecule from C$_{∞v}$ to C$_{2v}$ for the NH$_2^−$ ligand. In the CaNH$_2$ molecule, the A $^2Π$ state of CaF is further split into an in-plane (A $^2B_2$ state) and an out-of-plane ($B^2B_1$) state (Fig. 1). The energy ordering of the $\tilde{A}$ and $\tilde{B}$ states can be deduced using a simple argument. There is a lone pair of electrons in a nitrogen 2 $p_x$ orbital perpendicular to the plane of the NH$_2^−$ ligand. If the lone electron “belonging” to Ca$^+$ occupies the 4$p\pi$ ($B^2B_1$) orbital which is also perpendicular to the molecular plane, there will be greater electron–electron repulsion than if the lone electron occupied the 4$p\pi$ orbital.
The calculation of the dipole moments are in very good agreement with the ground state experimental dipole moments [for CaOH and SrOH (Ref. 35)] which were not available to them at the time of publication. A natural extension of this work would be to carry out similar calculations for non-linear ligands such as NH₂.

The first spectroscopic investigation of CaNH₂ was completed by Wormsbecher et al. in a Broida oven. A partial analysis of the 0⁰ band of the C₂A₁–X₂A₁ transition was carried out but our measurements on cold CaNH₂ molecules are not completely consistent with their reported line positions. Whitham et al.37 used the laser ablation/molecular beam technique to produce CaNH₂ but their studies were limited by the resolution of the probe laser (0.15 cm⁻¹) and consequently, only a partial analysis of the 0⁰ bands of the A₂B₂–X₂A₁ and B₂B₁–X₂A₁ systems was performed. Marr et al.38 recorded the first fully resolved high resolution spectrum of CaNH₂. They recorded the 0⁰ band of the A₂B₂–X₂A₁ system, from which they derived rotational constants and measured the dipole moments of the A and X states. The 0⁰ band of the B₂B₁–X₂A₁ system was analyzed by Zhao et al.,39 we report here a high resolution analysis of the 0⁰ bands of the C₂A₁–X₂A₁ band system. CaNH₂ is the first non–linear alkaline earth derivative where all four of the (X, A, B, C) low–lying electronic states are characterized at high resolution, thus we shall discuss the application of the simple “pure precession” model to polyatomic systems of low symmetry.

II. EXPERIMENT

CaNH₂ was produced using a pulsed laser ablation supersonic molecular beam spectrometer. Details of the experimental setup were provided in a previous paper (Zhao et al.,40) with the exception that a skimmer was not used in the experiments described here. Briefly, a rotating calcium rod was vaporized with the second harmonic of a pulsed Nd:YAG laser and approximately 5% NH₃ seeded in Ar (or He) was allowed to react with the metal vapor. A backing pressure of 50 psi was maintained behind the pulsed valve (General Valve). The probe laser, an argon ion pumped Coherent 699-29 cw ring dye laser (R6G dye), was crossed with the molecular beam ~15 cm downstream from the nozzle. The laser–induced fluorescence signal was viewed through a 600 nm ± 5 nm bandpass filter and focused onto a cooled GaAs photomultiplier tube.

A boxcar averager was used to gate the signal and for the experiment using Ar seed gas, the boxcar delay was 200 µs after the YAG pulse, while a 85 µs delay was used for the He experiment. In both experiments the boxcar gate was open for ~20 µs. The LIF signal was monitored in 50 MHz steps of the probe laser which was scanned at a rate of 60 seconds per 10 GHz. Typical linewidth (full width at half maximum) was of the order of 150–200 MHz. Calibration of the laser was achieved by simultaneously recording the laser excitation spectrum of I₂,41,42 giving an absolute accuracy of ±0.0035 cm⁻¹ for the measured line positions.
The allowed transition of the $K'_a = 1 \rightarrow K''_a = 1$ sub-band of the $\tilde{C}\,^2A_1 - \tilde{X}\,^2A_1$ transition. Each transition is labeled by $\Delta J'_{g'f'}(i=1,2)$, see text for details.

Figure 4.

III. OBSERVATIONS

The approximate positions of the $\tilde{A}\,^2B_2 - \tilde{X}\,^2A_1$, $\tilde{B}\,^2B_1 - \tilde{X}\,^2A_1$ and $\tilde{C}\,^2A_1 - \tilde{X}\,^2A_1$ band origins were known from the low resolution work of Bopegdera et al. and also from Wormsbecher et al. Thus, the laser was scanned at high resolution from 17 365 cm$^{-1}$ to 17 395 cm$^{-1}$ to measure the spectrum of the $\tilde{C}\,^2A_1 - \tilde{X}\,^2A_1$ system. Rotational structure of the spectrum was consistent with the parallel band structure of an a-type transition. The selection rules for a doublet a-type transition are $\Delta K_a = 0$, $\Delta K_c = \pm 1$, $\Delta J = \pm 1$, $F_1 \rightarrow F_1$, $F_2 \rightarrow F_2$ for a $K'_a = 0 \rightarrow K''_a = 0$ sub-band, while for a $K'_a = 1 \rightarrow K''_a = 1$ sub-band a Q-branch ($\Delta J = 0$) is also allowed. It is useful to introduce the label, $\gamma$, for the rotational energy levels (Jarman et al.), where $\gamma = K_a + K_c - N$, and $\gamma$ can take values of 0 or 1. Therefore, we can have $\gamma' = 0 \rightarrow \gamma'' = 0$ for a $K_a = 0 \rightarrow 0$ sub-band and both $\gamma' = 0 \rightarrow \gamma'' = 0$ and $\gamma' = 1 \rightarrow \gamma'' = 1$ for a $K_a = 1 \rightarrow 1$ sub-band.

The allowed transitions of the $K_a = 0 \rightarrow 0$ sub-band are depicted in Fig. 3. Each rotational level labeled $N_{K_a,K_c}$ is split into two fine structure levels by spin–rotation interactions, and are labeled $F_1$ for $J = N + \frac{1}{2}$ and $F_2$ for $J = N - \frac{1}{2}$. Only P and R branches for the $K_a = 0 \rightarrow 0$ sub-band are allowed so the rotational spectrum is analogous to a $2\Sigma - 2\Sigma$ transition of a diatomic molecule. Figure 4 shows the corresponding energy level diagram for a $K_a = 1 \rightarrow 1$ sub-band. In this case each rotational level is split into four components because of spin–rotation interactions ($F_1$ and $F_2$) and also due to asymmetry doubling ($\gamma = 0$ or 1, indicated by a superscript). Thus, the $K_a = 1 \rightarrow 1$ sub-band resembles a Hund’s case (b) $^{1} \Pi$—Hund’s case (b) $^{3} \Pi$ transition of a diatomic molecule.

Figure 5 shows the overview of the $\tilde{C} - \tilde{X}$ band system recorded in Ar and in He. The He spectrum has a slightly higher rotational temperature ($T_{rot} = 13$ K) than the Ar spectrum ($T_{rot} = 6$ K). Initially the Ar spectrum was used for data analysis, but the $F_2$ component of the $K_a = 1 \rightarrow 1$ sub-band was absent. Subsequently the higher temperature He spectrum was used for the analysis and we were able to obtain $J$ values as high as 19 $\frac{1}{2}$ for the $K_a = 0 \rightarrow 0$ sub-band and $J = 14 \frac{1}{2}$ for the $K_a = 1 \rightarrow 1$ sub-band. Some of the assigned transitions of the spectrum are shown in Figure 6. All of the allowed branches (4 for $K_a = 0 \rightarrow 0$, 12 for $K_a = 1 \rightarrow 1$) were seen in this spectrum, however, it was found that the transitions involving the $F_2$ component of the $K_a = 1 \rightarrow 1$ sub-band were very weak.

IV. RESULTS

The $\tilde{C} - \tilde{X}$ band system is an a-type transition so that the transition dipole moment is along the Ca–N bond. The $\Delta K_a = 0$ selection rule means that all of the sub–bands with different $K_a$ will have approximately the same origin, leading to a very congested spectrum. Fortunately, with the rotational cooling in a molecular beam only two $K_a$ values had
significant population \( (K_a = 0, 1) \). Because of nuclear spin statistics, the \( K_a = 1 \) rotational levels (ortho) cannot cool into the \( K_a = 0 \) (para) levels. Preliminary experiments, performed at Waterloo using a Broida oven showed that the spectrum of the \( \tilde{C} - \tilde{X} \) system was extremely dense, with many \( K_a \)-rotational sub-bands and vibrational hot bands present. The spectra recorded in this way were found to be extremely difficult to analyze.

The analysis of the \( \tilde{C} - \tilde{X} \) spectrum was partially aided by a Loomis–Wood program to sort out the branches. Although
this procedure is extremely useful in the analysis of congested spectra of \( ^1\Sigma \) diatomic molecules, more care must be taken with non–linear molecules and non–1 \( ^1\Sigma \) diatomics. This is because the line spacing of \( \rho \) and \( \rho \) branches that are connected can be quite different. For \( \text{CaNH}_2 \), a particular \( \rho \) or \( \rho \) branch can be found rather easily, but connecting the \( \rho \) and \( \rho \) branches was difficult. With the help of the spectroscopic constants of Marr et al., \(^{38}\) ground state combination differences were used to connect the branches. Once a single branch of the \( K_a'=0-K_a''=0 \) sub-band was assigned and fitted with a non–linear least squares program, the remaining branches were then assigned by prediction. The same procedure was used to assign the lines of the \( K_a'=1-K_a''=1 \) sub-band.

The data were fit using the effective rotational Hamiltonian (A–reduction) of Watson\(^{45}\) and the spin–rotation Hamiltonian of Brown et al.\(^{46}\) The spin–rotation Hamiltonian is written as:

\[
\hat{H}_a = \frac{1}{\hbar} \sum_{a,b} \epsilon_{a,b} (\hat{N}_a \hat{S}_b + \hat{S}_b \hat{N}_a),
\]

where \( \alpha \) and \( \beta \) are the principal rotation axes. A total of nine spin rotation constants are possible, but for a molecule with orthorhombic \( (C_{\text{2v}}) \) symmetry only three, \( \epsilon_{aa}, \epsilon_{bb} \), and \( \epsilon_{cc} \), are non-zero. It will be shown (see below) that these constants are determined by second order spin–orbit interactions rather than true spin–rotation interactions. The matrix elements used in the non–linear least squares program were taken from the literature (Watson,\(^{47}\) Hirota\(^{48}\)). For the \( \tilde{A}^2B_2-\tilde{X}^2A_1 \) lines of Marr et al.\(^{38}\) the \( \tilde{B}^2B_1-\tilde{X}^2A_1 \) lines of Zhao et al.\(^{39}\) were added to this data set\(^{49}\) and a global fit of all the data was done. The rotational constants for the \( \tilde{X}^2A_1, \tilde{A}^2B_2, \tilde{B}^2B_1, \tilde{C}^2A_1 \) states are reported in Table I.

### V. DISCUSSION

#### A. Pure precession model

The most interesting of the spectroscopic constants listed in Table I are the spin–rotation constants (\( \epsilon_{aa} \)). This is because we can use the simple pure precession model to give a physical picture of the orbitals containing the unpaired electron. \( \text{CaNH}_2 \) is the first of the alkaline earth polyatomic molecules for which all of the low–lying electronic states are known so a discussion of the pure precession is warranted.

In this model we will assume that only pure \( p \)–type orbitals give rise to the first three excited electronic states (Fig. 2) of \( \text{CaNH}_2 \) while the ground state has the unpaired electron in an \( s \)–type orbital.

The theory of spin–rotation interactions was first considered by Van Vleck.\(^{50}\) There are two major contributions to these parameters, a direct magnetic coupling between the electronic spin and molecular rotation, and a second order spin–orbit coupling between the electron spin and the unquenched angular momentum of the unpaired electron.\(^{51}\) It has been shown (Curl,\(^{52}\) Dixon\(^{53}\)) that the major contribution to the spin–rotation constants is the second order spin–orbit interaction.

The Hamiltonian for rigid rotation of a polyatomic molecule in the molecular frame with the inclusion of spin–orbit interaction is written as:

\[
\hat{H} = A(\hat{N}_a - \hat{L}_a)^2 + B(\hat{N}_b - \hat{L}_b)^2 + C(\hat{N}_c - \hat{L}_c)^2 + \sum_j \hat{\gamma}_j \hat{\gamma}_j,
\]

Here \( \hat{N} \) is the total angular momentum excluding spin, \( \hat{L} \) is the electronic angular momentum, \((a,b,c)\) are the principal axes in the molecular frame and the sum \( j \) is over all electrons in the system. From equation (2) we can see that the purely rotational part of the Hamiltonian is:

\[
\hat{H}_\text{rot} = A\hat{N}_a^2 + B\hat{N}_b^2 + C\hat{N}_c^2,
\]

and the perturbation of strict rigid rotation arises from the cross terms between:

\[
\hat{H}_1 = -2A\hat{N}_a\hat{L}_a + 2B\hat{N}_b\hat{L}_b - 2C\hat{N}_c\hat{L}_c
\]

and

\[
\hat{H}_2 = \sum_j \hat{\gamma}_j \hat{\gamma}_j.
\]

#### TABLE I. Spectroscopic constants for CaNH \(_2\) (cm\(^{-1}\)).

<table>
<thead>
<tr>
<th>( T_{0-0} )</th>
<th>( \tilde{X}^2A_1 )</th>
<th>( \tilde{A}^2B_2 )</th>
<th>( \tilde{B}^2B_1 )</th>
<th>( \tilde{C}^2A_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15464.3673(48)</td>
<td>15885.2818(99)</td>
<td>17375.1668(67)</td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} (B + C) )</td>
<td>0.9306(21)</td>
<td>0.301693(21)</td>
<td>0.301512(15)</td>
<td></td>
</tr>
<tr>
<td>( \frac{1}{2} (B - C) )</td>
<td>1.8894(44) ( \times 10^{-3} )</td>
<td>1.958(28) ( \times 10^{-3} )</td>
<td>4.6879(9) ( \times 10^{-3} )</td>
<td>1.7710(10) ( \times 10^{-3} )</td>
</tr>
<tr>
<td>( \epsilon_{aa} )</td>
<td>0</td>
<td>8.2369(12)</td>
<td>-7.5472(19)</td>
<td>0.9986(61)</td>
</tr>
<tr>
<td>( \frac{1}{2} (\epsilon_{ab} + \epsilon_{cc}) )</td>
<td>8.515(672) ( \times 10^{-4} )</td>
<td>3.0534(17) ( \times 10^{-2} )</td>
<td>2.083(13) ( \times 10^{-2} )</td>
<td>-3.9134(10) ( \times 10^{-2} )</td>
</tr>
<tr>
<td>( \frac{1}{2} (\epsilon_{ab} - \epsilon_{cc}) )</td>
<td>0</td>
<td>-1.2617(14) ( \times 10^{-2} )</td>
<td>-8.66(17) ( \times 10^{-3} )</td>
<td>-3.28(175) ( \times 10^{-4} )</td>
</tr>
<tr>
<td>( D_K )</td>
<td>-</td>
<td>-</td>
<td>-4.040(29) ( \times 10^{-2} )</td>
<td>-</td>
</tr>
<tr>
<td>( D_N )</td>
<td>-</td>
<td>-</td>
<td>-1.09(13) ( \times 10^{-6} )</td>
<td>1.088(25) ( \times 10^{-6} )</td>
</tr>
<tr>
<td>( \delta_K )</td>
<td>-</td>
<td>-</td>
<td>2.160(74) ( \times 10^{-3} )</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta_K^a )</td>
<td>-</td>
<td>-6.065(30) ( \times 10^{-2} )</td>
<td>-1.46(17) ( \times 10^{-2} )</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta_K^b )</td>
<td>-</td>
<td>-6.67(16) ( \times 10^{-2} )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta_K^c )</td>
<td>-</td>
<td>5.90(17) ( \times 10^{-3} )</td>
<td>2.54(20) ( \times 10^{-3} )</td>
<td>-</td>
</tr>
</tbody>
</table>
Performing a Van Vleck transformation leads to the effective spin-rotation Hamiltonian for a molecule with $C_{2v}$ symmetry:

$$\hat{H}_u = \epsilon_{aa}\hat{N}_a \hat{S}_a + \epsilon_{bb}\hat{N}_b \hat{S}_b + \epsilon_{cc}\hat{N}_c \hat{S}_c,$$

(5)

neglecting the quartic spin-rotation terms (for example see Duxbury\textsuperscript{51} or Brown et al.\textsuperscript{46}). It was shown by Dixon\textsuperscript{53} that the second order spin–orbit corrections to the spin–rotation constants of a doublet state are:

$$\epsilon_{aa}^{(2)} = \sum_{n \neq 0}^{\infty} \sum_j \frac{4B_\alpha k_j \langle \psi_0 | \hat{\Gamma} | \psi_n \rangle \langle \psi_n | \hat{\Gamma} \psi_{a,n} \rangle \langle \psi_{a,n} | \psi_0 \rangle}{E_n^0 - E_0^0}.$$  

(6)

The sum $j$ is over all electrons, $k_j = \pm 1$ for promotion of an unpaired electron, $k_j = -1$ for promotion of an electron into a half–filled orbital or zero otherwise. The $B_{\alpha}$'s in (6) are the rotational constants in the principal axis system (e.g. $B_a = A$, $B_b = B$, $B_c = C$). The matrix element involving $\hat{\Gamma}_{a,n}$ can be written in terms of the one–electron orbital angular momentum operators, $\hat{\Gamma}_{a,n} = \xi_j \hat{\rho}_j$, where $\xi_j$ is the spin–orbit constant for the electron. In the pure precession limit, we can neglect all electrons except the unpaired valence electron on Ca\textsuperscript{11}. Thus we can remove the sum over $j$ with a single term involving $\xi_j \hat{\rho}_j$ leaving the second order correction to the spin–rotation constants as:

$$\epsilon_{aa}^{(2)} = \sum_{n \neq 0}^{\infty} \frac{4B_\alpha \langle \psi_0 | \hat{\Gamma} | \psi_n \rangle \langle \psi_n | \hat{\Gamma} \psi_{a,n} \rangle \langle \psi_{a,n} | \psi_0 \rangle}{E_n^0 - E_0^0}.$$  

(7)

A similar analysis as above can be done for the second order correction to the rotational constants (A,B,C). The result is:

$$B_{\alpha}^{(2)} = \sum_{n \neq 0}^{\infty} \frac{4B_\alpha^2 \langle \psi_0 | \hat{\Gamma} | \psi_n \rangle \langle \psi_n | \hat{\Gamma} \psi_{a,n} \rangle \langle \psi_{a,n} | \psi_0 \rangle}{E_n^0 - E_0^0}.$$  

(8)

It will be shown later that the second order correction to the $A$ rotational constant is significant while the corrections to $B$ and $C$ are negligible.

A second simplification that can be made is the unique perturber approximation, where we assume that each electronic state interacts solely with a dominant perturbing state (Dixon\textsuperscript{54}). In CaNH\textsubscript{2}, rotation of the molecule about the a–axis causes interactions between the $\bar{B}^2 B_1$ ($\rho_x$) and $\bar{A}^2 B_3$ ($\rho_y$) states, rotation about the c–axis causes interactions between the $\bar{C}^2 A_1$ ($\rho_z$) and the $\bar{B}^2 B_1$ states and finally, rotation about the b–axis leads to interactions of the $\bar{C}^2 A_1$ and $\bar{A}^2 B_3$ states.

To obtain the second order correction of $\epsilon_{aa}$ in the $\bar{A}^2 B_3$ state, one needs wavefunctions for the two interacting states ($\bar{B}^2 B_1$, $\bar{A}^2 B_3$) and the integrals $\langle \bar{B}^2 B_1 | \hat{\Gamma}_a | \bar{A}^2 B_3 \rangle$, $\langle \bar{A}^2 B_3 | \xi_j \hat{\rho}_j | \bar{B}^2 B_1 \rangle$ need to be evaluated. However, in the pure precession limit we assume that the electronic states arise strictly from pure $p$–type orbitals. In Table II, the correlation of the electronic states and the principal axis system with the (x,y,z) coordinate system is provided. Table III shows the effect of the one-electron orbital angular momentum operators on the three $p$–orbitals. Using these results and equation (7) we can write the formula for the second order correction to $\epsilon_{aa}$ of the $\bar{A}^2 B_3$ state as:

$$\epsilon_{aa}^{(2)} = \frac{4A \langle \rho_x | \hat{\Gamma}_a | \rho_y \rangle \langle \rho_y | \xi_j \hat{\rho}_j | \rho_x \rangle}{E_B^0 - E_A^0} - \frac{4A \xi_j \rho_z}{E_B^0 - E_A^0}.$$  

(9)

In the last step we replace $\xi_j \rho_z$ with $A^{\infty}$, which is the spin–orbit splitting in the hypothetical linear molecule. Clearly one can see that we get the negative of equation (9) for $\epsilon_{bb}$ of the $\bar{B}^2 B_1$ state. Performing similar calculations we get $\epsilon_{bb}^{(2)} = 0$ for the $\bar{A}^2 B_3$ state, $\epsilon_{cc}^{(2)} = 0$ for the $\bar{C}^2 A_1$ state and:

$$\epsilon_{bb}^{(2)} = \pm \frac{4BA^{\infty}}{E_C^0 - E_B^0}, \quad \epsilon_{cc}^{(2)} = \pm \frac{4CA^{\infty}}{E_C^0 - E_A^0}.$$  

(10)

In the above formulae the top sign corresponds to the lower electronic state of the interacting pair of states. The second order correction to the A rotational constant then becomes:

$$A^{(2)} = \pm \frac{4A^2}{E_B^0 - E_A^0}.$$  

(11)

One can see the close connection between the above results and the perturbation treatment of Whitham and Junger.\textsuperscript{37} They considered the rotation about the a–axis as equivalent to an a–axis Coriolis interaction with an off–diagonal spin–orbit coupling. The Hamiltonian for this interaction is:

$$\hat{H}_{\text{int}} = A^{\infty} \hat{\Gamma}_a \hat{S}_a - 2A \hat{N}_a \hat{\Gamma}_a.$$  

(12)

The a–axis of a (near) prolate symmetric top molecule plays the same role in quantization as the internuclear axis of a diatomic molecule so they replaced the angular momentum operators $\hat{N}_a$, $\hat{\Gamma}_a$, $\hat{S}_a$ by their corresponding quantum numbers $K_a$, $\Lambda$ and $\Sigma$. They then diagonalized the $2 \times 2$ energy matrix for the interacting $\bar{A}$ and $\bar{B}$ states, and solved for the correction to their energies to second order. The relevant results from their analysis are:

<table>
<thead>
<tr>
<th>$\hat{\Gamma}_x$</th>
<th>$\hat{\Gamma}_y$</th>
<th>$\hat{\Gamma}_z$</th>
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<tr>
<td>$\rho_x$ = 0</td>
<td>$\rho_y$ = $-i\rho_z$</td>
<td>$\rho_z$ = $i\rho_y$</td>
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<tr>
<td>$\rho_y$ = $ip_x$</td>
<td>$\rho_z$ = 0</td>
<td>$\rho_z$ = $-i\rho_y$</td>
</tr>
<tr>
<td>$\rho_z$ = $-ip_x$</td>
<td>$\rho_z$ = $ip_y$</td>
<td>$\rho_z$ = 0</td>
</tr>
</tbody>
</table>

(13)
The formula for \(\epsilon_{aa}^{(2)}\) is equivalent to the formula derived from the pure precession limit where we had already used the fact that \(\Lambda = 1\) (\(\Lambda\) being the projection of the electronic orbital angular momentum on the top axis) for a \(p\)–orbital. \(A_{spec}\) is the rotational constant derived from fitting the line positions of the spectra, and again the top sign of equation (13) refers to the lower electronic state. This result also shows that the observed value of the \(A_{spec}\) rotational constant contains a large second order contribution to the true \(A\) rotational constant.

On the basis of the molecular geometry, \(\Delta A = A_{spec}^B - A_{spec}^A\) should be small since the electron occupies an in–plane or an out–of–plane “non-bonding” \(p\)–orbital. However, there is a significant difference between the \(A\)’s (\(A_{spec}^A = 11.449\) cm\(^{-1}\) and \(A_{spec}^B = 14.366\) cm\(^{-1}\)) which would at first sight imply a large change in geometry. Applying the second order correction from equation (13) we find that the true rotational constant for the \(\tilde{A}\) and \(\tilde{B}\) states is 12.907 cm\(^{-1}\), which is very close to the \(A_{spec}^B = 12.951\) cm\(^{-1}\) for the \(\tilde{C}\) state and to the \(A_{spec}^A = 13.057\) cm\(^{-1}\) of the ground state. The second order corrections to the \(B\) (where \(B^{(2)} = \pm (4B/2(E_{\tilde{C}} - E_{\tilde{A}}))\) and \(C\) rotational constants are small (\(\sim 10^{-4}\) cm\(^{-1}\)) compared to experimental uncertainty of these constants.

The approach given by Whitham and Jungen is specific to the \(\tilde{A}\) and \(\tilde{B}\) states and interactions about the \(a\)–axis. Our discussion here is more general and for an electron that possesses a well defined orbital angular momentum we can write effective formulae for \(\epsilon_{bb}\) and \(\epsilon_{cc}\):

\[
\epsilon_{bb}^{(2)} = \pm \frac{2\sqrt{(\Lambda + 1)}BA_{spec}^{\infty}}{E_{\tilde{C}} - E_{\tilde{B}}}, \quad \epsilon_{cc}^{(2)} = \pm \frac{2\sqrt{(\Lambda + 1)}CA_{spec}^{\infty}}{E_{\tilde{C}} - E_{\tilde{A}}},
\]

where \(\sqrt{\Lambda} = 1\) for \(p\) orbitals.

The comparison of the observed spin–rotation contents to their corresponding pure precession values are shown in Table IV. The values calculated from the pure precession formula are in reasonable agreement with the observed spin rotation parameters in both magnitude and sign. The \(\epsilon_{aa}\) parameter is well predicted in the \(\tilde{A}, \tilde{B}\) states, i.e. within 10% of the experimental value. Also, the spin–rotation parameters in the ground state are predicted to be zero by pure precession and experimentally we find an extremely small value for \(3\epsilon_{bb} + 5\epsilon_{cc}\). For a ground state that correlates to a \(2\Sigma^+\) state in a linear configuration, the expected spin rotation parameter, \(\gamma\), would be small. Since \(\frac{3\epsilon_{bb} + 5\epsilon_{cc}}{2}\) is equivalent to \(\gamma\) of a linear molecule, the size of \(\frac{3\epsilon_{bb} + 5\epsilon_{cc}}{2} = 0.0385\) cm\(^{-1}\) should be close to that of CaOH (\(\gamma = 8.5 \times 10^{-4}\) cm\(^{-1}\)) or CaF (\(\gamma = 9.53 \times 10^{-4}\) cm\(^{-1}\)). The parameter \(\epsilon_{aa}\) is equivalent to the spin–orbit (\(A\)) constant of a linear molecule, which is zero for a \(2\Sigma^+\) state. The other spin–rotation parameters of Table IV are in good qualitative agreement with the pure precession values except for \(\epsilon_{aa}\) of the \(\tilde{C} 2\) state and \(\epsilon_{bb}\) of the \(\tilde{B} 2\) state. This is most likely due to mixing of the pure \(p\)–orbitals (assumed in our pure precession model) with \(d\)–orbitals. This is further supported by the higher order quartic spin–rotation parameters (\(\Delta X^3, \Delta Y^3, \Delta Z^3\)) that are required to adequately fit the transitions to the \(\tilde{B} 2\) state.

Finally, we have calculated values for the \(g\)–tensor from C útil’s formula:

\[
g_{aa} = g_e - \frac{\epsilon_{aa}}{2B_a},
\]

where \(g_e\) is the electron \(g\)–factor. The predicted values are reported in Table V.
TABLE VI. Geometrical parameters.

<table>
<thead>
<tr>
<th></th>
<th>$\tilde{X}^2A_1$</th>
<th>$\tilde{A}^2B_2$</th>
<th>$\tilde{B}^2B_1$</th>
<th>$\tilde{C}^2A_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{\text{NH}}$ (°)</td>
<td>100.5°</td>
<td>101.3°</td>
<td>101.3°</td>
<td>101.1°</td>
</tr>
<tr>
<td>$r_{\text{NH}}$ (Å)</td>
<td>1.041</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{\text{CaN}}$ (Å)</td>
<td>2.118</td>
<td>2.098</td>
<td>2.123</td>
<td>2.102</td>
</tr>
<tr>
<td>$\theta_{\text{NH}}$ (°)</td>
<td>102.9°</td>
<td>103.8°</td>
<td>103.8°</td>
<td>103.5°</td>
</tr>
<tr>
<td>$r_{\text{CaN}}$ (Å)</td>
<td>2.140</td>
<td>2.120</td>
<td>2.125</td>
<td>2.125</td>
</tr>
</tbody>
</table>

*Bond distance from NH$_2^-$, Ref. 56.

B. Geometrical parameters

We have calculated $r_0$ geometries for all of the low-lying states of CaNH$_2$. Rotational constants are available for only one isotopomer ($^{40}$Ca$^{14}$NH$_2$), so that all three structural parameters $r_{\text{CaN}}$, $r_{\text{NH}}$, and $\theta_{\text{NH}}$ cannot be determined simultaneously for the planar CaNH$_2$ molecule. The inertial defects are 0.16, 0.13, 0.45 and 0.01 amu Å$^2$ for the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$ and $\tilde{C}$ states, respectively. Thus, the $r_{\text{NH}}$ bond distance was constrained to the value found in NH$_2$ (Ref. 56) $r_{\text{NH}}=1.041$ Å or NH$_2$ (Ref. 57) $r_{\text{NH}}=1.023$ Å. For the $\tilde{A}$ and $\tilde{B}$ states we used the true value of the $\alpha$ rotational constant to calculate $I_\alpha$. Fundamental constants and molecular masses were taken from Ref. 58. In each case we calculated the geometry with $(I_A,I_B)$ or $(I_A,I_C)$ pairs. Table VI and VII show the results of the calculation, which are the average of the moment of inertia pairs, and these are compared with $r_e$ *ab initio* calculations$^{50}$ performed for CaNH$_2$. The theoretical values are in reasonable agreement with experiment, except for the HNH angle.

VI. CONCLUSIONS

The high resolution spectrum of the $\tilde{C}^2A_1$–$\tilde{X}^2A_1$ band system of CaNH$_2$, has been recorded and analyzed. CaNH$_2$ is the first alkaline–earth polyatomic molecule for which high resolution data are available for the first three excited states. We used the pure precession model to predict the spin–rotation parameters for this molecule. This model confirms the simple one–electron hydrogenic picture often used for diatomic alkaline–earth molecules but is also useful for nonlinear polyatomic molecules such as CaNH$_2$.

ACKNOWLEDGMENTS

This work is supported by Natural Sciences and Engineering Research Council of Canada (NSERC). Z. M. also wishes to thank NSERC for a graduate scholarship. We thank W. Chan and I. Hamilton for providing us with the results of their calculations in advance of publication.

TABLE VII. Experimental and *ab initio* parameters for the $\tilde{X}^2A_1$ state.

<table>
<thead>
<tr>
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<th>DFT *</th>
<th>Expt.</th>
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<td>$\theta_{\text{NH}}$ (°)</td>
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<td>1.041b</td>
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<tr>
<td>$r_{\text{CaN}}$ (Å)</td>
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<td>2.118</td>
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</table>

Vibration $^a$

<table>
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<th>DFT (cm$^{-1}$)*</th>
<th>Expt. (± 10 cm$^{-1}$)*</th>
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<tr>
<td>$\nu_6$ anti–symm. NH bend</td>
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<tr>
<td>$\nu_7$ out–of–plane bend</td>
<td>$b_1$</td>
<td>455</td>
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<tr>
<td>$\nu_5$ Ca–N stretch</td>
<td>$a_1$</td>
<td>544</td>
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<tr>
<td>$\nu_2$ symm. NH bend</td>
<td>$a_1$</td>
<td>1586</td>
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<tr>
<td>$\nu_1$ symm. NH stretch</td>
<td>$a_1$</td>
<td>3448</td>
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<tr>
<td>$\nu_3$ anti–symm. NH stretch</td>
<td>$b_2$</td>
<td>3535</td>
</tr>
</tbody>
</table>

*Reference 59.

*Fixed, see text.

*From low resolution Broida oven experiment.

49 See AIP document no. PAPS JCPSA-106-4860-3 for 3 pages of tables.

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58 I. Mills et al., Quantities, Units and Symbols in Physical Chemistry (Blackwell Scientific, Oxford, 1988).