A high-resolution analysis of the $\tilde{A} 2A'-\tilde{X} 2A'$ transition of CaSH by laser excitation spectroscopy

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The high resolution spectrum of the $\tilde{A} 2A'-\tilde{X} 2A'$ transition of CaSH has been recorded near 650 nm using laser excitation spectroscopy with selected fluorescence detection. While both $a$-type and $b$-type rotational transitions have been observed, extensive measurements have been made for the $b$-type transitions up to $K'_{a}=4$ and $K'_{b}=5$. Altogether over 3000 rotational lines have been measured and fitted with an $A$-reduced Hamiltonian. The $X 2A'$ state has rotational constants $A=9.693322(46)$ cm$^{-1}$, $B=0.1418647(33)$ cm$^{-1}$, and $C=0.1395810(33)$ cm$^{-1}$. The $\tilde{A} 2A'$ state has a band origin at 15 380.2847(2) cm$^{-1}$, and effective values for the rotational constants $A=9.090808(78)$ cm$^{-1}$, $B=0.1474598(34)$ cm$^{-1}$, and $C=0.1448047(34)$ cm$^{-1}$. An approximate $r_0$ structure for CaSH is discussed.

The $\tilde{A} 2A'$ state is the lower energy Renner-Teller component of the $\tilde{A} 2II$ state of the hypothetical linear CaSH molecule, and consequently was found to have a relatively large positive value for the spin--rotation parameter $\epsilon_{a}\epsilon_{b}/2$ at 3.44569(26) cm$^{-1}$. The upper asymmetry component of the $F_\frac{1}{2}$ spin component of the $K_{a}=1$ stack and the $F_3$ spin component of the $K_{a}=0$ stack in the $\tilde{A} 2A'$ state perturb each other with an avoided crossing between $J=37.5$ and $J=38.5$. These two spin components interact through the off-diagonal $|\epsilon_{a}\epsilon_{b}|/2$ element of the spin--rotation tensor. For CaSH, the $\tilde{A} 2A'$ state has $|\epsilon_{a}\epsilon_{b}|/2=0.065915(46)$ cm$^{-1}$.

INTRODUCTION

In contrast to the extensive amount of research work devoted to the high resolution spectroscopic study of gas phase alkaline earth monohydroxides\textsuperscript{1-9} in recent years, there has been only one low resolution spectroscopic investigation of the isovalent monohydrosulfides.\textsuperscript{10} The parent dihydrosulfides are important in industrial processes—an aqueous solution of Ca(SH)$_2$ has been used both in the removal of SO$_2$ and SO$_3$ from H$_2$SO$_4$ (Ref. 11) and also in the recovery of sulfur from underground ore deposits.\textsuperscript{12} The nature of the metal–sulfur bond is also important to the inorganic chemist and in the study of biological systems such as the active sites of proteins. It is clear, therefore, that a more detailed probe of the structures and properties of metal containing sulfur compounds is desirable.

The previous spectroscopic study of CaSH by Fernando et al.,\textsuperscript{10} approximate term energies and Ca–S stretching frequencies were determined from low resolution spectra for the ground and the three lowest excited electronic states. The values they obtained were in good agreement with the \textit{ab initio} electron propagator calculations of Ortiz.\textsuperscript{13} However, the low resolution spectra did not provide any means to unequivocally determine the symmetry or geometry of the electronic states. Some of this information came from a preliminary investigation of the $B 2A''-\tilde{X} 2A'$ transition at high resolution by Ram and Bernath.\textsuperscript{14} In the work reported here, we have concentrated on recording and analyzing the lowest-lying $\tilde{A} 2A'-\tilde{X} 2A'$ transition.

According to Ortiz's \textit{ab initio} calculations,\textsuperscript{13} the $\tilde{A} 2A'$ and $B 2A''$ states of CaSH are well described by a one electron picture in which the unpaired electron is localized near the Ca atom in a calcium centered orbital of approximate $p_x$ symmetry. This orbital is slightly hybridized away from the SH ligand by mixing with calcium $d_z$ functions. The $\tilde{A} 2A'$ state corresponds to the component of the $p_x$ orbital in the plane of the molecule, and the $B 2A''$ state corresponds to the out-of-plane component. Since CaSH is bent, the in-plane $p_x$ and the out-of-plane $p_y$ orbitals have different energies. Molecular rotation about the $a$ axis will cause these two states to mix and hence induce some $K_a$ dependent orbital angular momentum into both of these states. The magnitude of this orbital momentum will be determined by the energy separation between the $\tilde{A} 2A'$ and $B 2A''$ states. A similar effect has been discussed by Whitham and Jungen\textsuperscript{15} in their study of the corresponding states of CaNH$_2$.

EXPERIMENT

CaSH was produced in a conventional Broida oven\textsuperscript{16} by the reaction of excited Ca atoms with H$_2$S. Two lasers were used in this study, one to promote the chemical reaction by exciting a Ca atomic transition, and another to probe the molecular transitions. The first laser was a Coherent 699-01 dye laser pumped by 6 W of all lines visible radiation from a Coherent Innova 70 argon ion laser and

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The Laser Excitation Spectrum of CaSH

FIG. 1. The low resolution laser excitation spectrum of CaSH. The features marked with asterisks are the two spin components of the \( \tilde{A}^2 \Sigma^+ \rightarrow \tilde{X}^2 \Sigma^+ \) transition of CaOH, produced as an impurity. The feature at 610 nm is due to transitions to one quantum in the Ca-S stretch of the \( \tilde{C}^2 \Pi \) state.

Operating in linear mode with DCM dye. The bandwidth of this laser was narrowed (triple mode operation) with an étalon, and the laser was tuned to the \( ^3 \Pi_{1/2} \rightarrow ^1 \Sigma^+ \) atomic transition of Ca at 657.3 nm. The laser beam was directed into the alumina crucible containing the Ca metal in the Brodhead oven. When \( \text{H}_2 \text{S} \) was added at the top of the crucible, a white chemiluminescent flame appeared characteristic of CaSH production.

The probe laser was a Coherent 699-29 ring dye laser operating with DCM dye and pumped by 7 W of 488 nm radiation from a Coherent Innova 200 argon ion laser. The laser beam was focused vertically into the CaSH flame, and the laser induced fluorescence was focused onto the entrance slits of a 0.64 m monochromator. Care was taken to separate the atomic pump laser beam from the molecular probe laser beam so that the entrance slits of the monochromator could act as a spatial filter and remove most of the Ca atomic fluorescence. The molecular laser induced fluorescence was then dispersed by the monochromator, detected with a photomultiplier tube, and processed by photon counting electronics.

Initially, we scanned the probe laser broad band (1 cm\(^{-1}\) resolution) and detected the laser induced fluorescence through the monochromator in zeroth order, effectively recording the total molecular fluorescence. The spectrum is depicted in Fig. 1, from which it is clear that the two lowest-lying electronic transitions \( \tilde{A}^2 \Pi \rightarrow \tilde{X}^2 \Pi \) and \( \tilde{B}^2 \Pi \rightarrow \tilde{X}^2 \Pi \) cover a wider spectral range than the third electronic transition \( \tilde{C}^2 \Pi \rightarrow \tilde{X}^2 \Pi \). We attribute this observation to larger amounts of perpendicular rotational structure in \( \tilde{A}^2 \Pi \rightarrow \tilde{X}^2 \Pi \) and \( \tilde{B}^2 \Pi \rightarrow \tilde{X}^2 \Pi \), compared to the parallel \( \tilde{C}^2 \Pi \rightarrow \tilde{X}^2 \Pi \) transition. This fact will make the \( \tilde{C}^2 \Pi \rightarrow \tilde{X}^2 \Pi \) transition very difficult to analyze because many \( \tilde{A} \)-type rotational transitions will lie in a small wavelength range. The spectrum also displays fluorescence from the \( \tilde{A}^2 \Pi \rightarrow \tilde{X}^2 \Sigma^+ \) system of CaOH, produced as an impurity.

We then scanned the probe laser at high resolution, and recorded selected pieces of the spectrum near 650 nm as a function of wave number using Coherent's PC-Autoscan software. These scans had a high signal-to-noise ratio, but the incredible density of molecular lines made them difficult to interpret. However, certain features in these spectra were stronger than others and looked as if they might be bandheads. Our next step was to record dispersed fluorescence spectra by fixing the probe laser on each of these bandhead features in turn, and scanning the monochromator for each laser position. The majority of the dispersed fluorescence in these spectra was resonant and all the scans contained a resonant feature near 650 nm, one resonant feature to higher wavelength, and one to lower wavelength. We concluded that we were seeing an \( ab \) hybrid rovibronic transition between two bent electronic states with similar \( \tilde{A} \) rotational constants—the laser was probing different upper \( K_a \) stacks, and the fluorescence was obeying \( \Delta K_a = \pm 1,0 \) selection rules.

High resolution (1 MHz laser bandwidth) spectra were then recorded by fixing the monochromator on one of the resonant features found in a dispersed fluorescence spectrum and scanning the laser for 20 cm\(^{-1}\) around its original position. In this way, we could selectively record fluorescence from different upper \( K_a \) stacks. The Doppler-limited spectra were stored as a function of wave number using Coherent's PC-Autoscan software. The wave number scale was calibrated by simultaneously recording the iodine absorption spectrum and comparing the measured line positions to the published line list\(^{11}\) correcting for the \( -0.0056 \text{ cm}^{-1} \) shift.\(^{18}\) The high resolution data files were converted to ASCII format for use with the data reduction package PC-DECOMP developed at the National Solar Observatory by Braut. Each rovibronic line in the spectra was first fit to a Voigt profile using PC-DECOMP, and then the line positions and intensities were used as input to PC-LOOMIS, an interactive color Loomis-Wood\(^{19}\) program written by one of the authors (Jarman) to pick out rotational branches.

**ANALYSIS OF THE SPECTRA**

At first we recorded and analyzed only the \( b \)-type \( K_a \geq 2 \) transitions in which there was expected to be negligible asymmetry doubling. These spectra did indeed prove to be both the easiest to record and the easiest to analyze. The spectra were recorded by scanning the laser over the transitions with \( K''_a = K'_a - 1 \), while keeping the monochromator on the resonant bandheads with \( K''_a = K'_a + 1 \) (see Fig. 2). After recording these spectra, the positions of the laser and monochromator were switched to record \( \Delta K_a = -1 \) spectra. Because the laser and the monochromator positions are spaced by approximately \( \Delta K''_a/K'_a \) (e.g., \( \sim 80 \text{ cm}^{-1} \) for \( K'_a = 2 \)), we could open the monochromator slits without fear of seeing the laser. Thus the entire \( J \) structure of the bandhead could lie in the monochromator bandpass, and so the entire \( J \) structure for the connecting \( K'_a \) subband could be recorded in one scan.

The initial analysis of these spectra was simplified by the large value for the effective \( \tilde{A} \) rotational constant in both states. This allowed each \( K'_a \neq 0 \) stack to be treated, in
C. N. Jarman and P. F. Bernath: The $\tilde{A}^2A^\prime-\tilde{X}^2A^\prime$ transition of CaSH

first approximation, as an independent $^2\Pi$ state with a spin–orbit splitting of $\epsilon_{\alpha\beta}$ $K_\alpha$. It quickly became apparent by comparing different spectra that the value for $\epsilon_{\alpha\beta}$ in the ground state was zero, just as expected for an isolated state that correlates to a $^2\Sigma^+$ state in the linear configuration. By analogy with the ground states of CaOH, and CaF, the value for the spin-rotation constant $(\epsilon_{\alpha\beta} + \epsilon_{\alpha\gamma})/2 = \gamma$ ($\gamma''=0.0012$ cm$^{-1}$ for CaOH and $\gamma''=0.0013$ cm$^{-1}$ for CaF) was also expected to be small, and so the $F_1$ and $F_2$ components were expected to be almost coincident in energy. Thus the $K_\alpha=0$ stacks for the ground state were expected to behave like Hund’s case (b) $^2\Pi$ states. However, the value of $\epsilon_{\alpha\beta}$ in the upper state was found to be relatively large, and so the $K_\alpha=0$ stacks for the upper state were more like Hund’s case (a) $^2\Pi$ states. This is evident in Figs. 3 and 4, which show the two different spin components of the 4–3 subband. The energy separation between the $P_1 + Q_{12}$ and the $Q_2 + P_{21}$ bandheads is about 13 cm$^{-1}$, and this gives an approximate value for $\epsilon_{\alpha\beta}$ of $\sim 3.25$ cm$^{-1}$.

Thus the 4–3, 4–5, 3–4, 3–2, and 2–3 subbands were initially analyzed as separate $^2\Pi\Delta(a)-^2\Pi\Delta(b)$ electronic transitions of a diatomic molecule, with strong $Q_2$, $Q_1$, $R_2$, $R_1$, $P_2$, and $P_1$ branches, and weak $Q_{12}$, $Q_{12}$, $R_{21}$, $P_{21}$, $R_{12}$, and $P_{12}$ satellite branches. Most of these satellite branches, except $R_{21}$ and $P_{12}$, lay beneath stronger regular branches, and so the spectra displayed four distinct rotational branches in two separate regions split by the effective spin–orbit constant—$P_{21}$, ($Q_2$ and $P_{21}$), ($R_2$ and $Q_{21}$), and $R_{21}$ in one region, and $P_{12}$, ($P_1$ and $Q_{12}$), ($Q_{12}$, and $R_{12}$), and $R_{1}$ in the other. The satellite branches also became weaker as $K_\alpha$ went from 4 to 2, in keeping with the increasing Hund’s case (b) character (smaller effective spin–orbit splitting) of the lower $K_\alpha$ stacks.

Using this model, it was possible to assign $J$ quantum numbers to every rovibronic transition in the subbands, and to determine values for the effective spin–orbit constants in the upper $K_\alpha$ stacks. Because these values agreed very well with the $\epsilon_{\alpha\beta}K_\alpha$ formula, we next proceeded to fit these subbands together using a doublet asymmetric rotor Hamiltonian. The $A$-reduced rotational Hamiltonian of Watson$^{21}$ was used together with Brown and Sears$^{22}$ $A$-reduced form for the spin-rotation part of the Hamiltonian

$$
\begin{align*}
\tilde{H}_{kr}^{(2)} &= \epsilon_{\alpha\beta}N_\alpha S_\alpha + \epsilon_{\alpha\beta}N_\beta S_\beta + \epsilon_{\alpha\gamma}N_\gamma S_\gamma + 1/2(\epsilon_{ab} + \epsilon_{ba}) \\
& \times (N_\beta S_\gamma + N_\gamma S_\beta), \\
\tilde{H}_{kr}^{(4)} &= \Delta^2 N_\alpha^2 (N \cdot S) + 1/2\Delta^2 N_\gamma^2 (N_\alpha N_\beta S_\gamma + N_\beta N_\gamma S_\alpha + N_\gamma N_\alpha S_\beta) \\
& + \Delta^2 N_\alpha^2 N_\beta^2 (N \cdot S) + \Delta^2 N_\beta^2 N_\gamma^2 S_\gamma + \delta^2 (N_\alpha^2 + N_\beta^2) \\
& \times (N \cdot S) + 1/2\delta^2 [(N_\alpha^2 + N_\gamma^2) N_\beta S_\gamma + N_\beta S_\gamma (N_\alpha^2 + N_\gamma^2)].
\end{align*}
$$

A computer program was written that set up the Hamiltonian matrix in a total parity conserving basis set, using the matrix elements listed in Hirota’s book on free radicals.$^{23}$ In this fit, we deliberately excluded the high $J$ tran-
sitions of the 3–2 and 2–3 subbands, and constrained the off-diagonal matrix elements in \( K_\sigma \) to zero in both electronic states. The transitions fit very well and this augured well for the continuation of the analysis to lower \( K_\sigma \).

The next step was to record and analyze the 2–1 subband. This was easy, because we already knew the location of the connecting 2–3 bandheads. The assignment was relatively straightforward, and when we included this subband in our global fit, we determined values for the asymmetry in the rotational constants \( (B - C)/2 \) in the ground state. We then predicted the line positions for the 0–1 and the 0–0 subbands, but this prediction was not very accurate because it involved extrapolation from \( K_\sigma = 2 \) in the upper state. However, it did provide a good starting point to locate the bandheads, which in turn allowed us to scan the laser through the 0–0 and the 0–1 subbands with the monochromator on the bandheads in the connecting subband.

The rotational structure for \( K_\sigma = 0 \) in both the ground and excited states is very similar to that seen in a \( 2^2 \) state of a diatomic molecule, and hence the 0–0 subband looked like a \( 2^2 \) state with \( R_{22}, R_{11}, R_{21}, \) and \( P_{11} \) branches. The 0–1 subband looked like a \( 2^2 \) state with additional \( Q_{22}, Q_{11}, \) and satellite branches. Both of these subbands revealed that the \( K_\sigma = 0 \) stack was perturbed by a higher energy spin component cross-coupling below it between \( J = 37.5 \) and \( J = 38.5 \). Hence, we added to the data local set all of the \( K_\sigma = 0 \) transitions, but only transitions up to \( J = 19.5 \). We also included the high \( J \) \( K_\sigma = 2 \) transitions that we omitted from previous fits, fixed the value for \( (B - C)/2 \) in the upper state to the same as that for the ground state, and refit the data.

We then predicted and recorded the spectra for the 1–0, 1–1, and 1–2 subbands, using the same techniques that we used previously. However, because the spacing between the upper state spin components was only about 3.5 cm\(^{-1} \), it was impossible to record each component separately, and so the spectra were complicated by many overlapping rotational branches. The predictions were not very helpful in sorting out the mess because the energies of the \( K_\sigma = 1 \) spin components depend on the first order corrections of the off-diagonal \( \Delta K_\sigma = \pm 2 \) matrix elements. We had made a reasonable guess for the value of \( (B - C)/2 \), but had no idea of the value or even the sign for the \( \epsilon_{bb} - \epsilon_{cc} \) parameter associated with the \( \Delta K_\sigma = \pm 2 \) matrix elements. The \( J \) assignment was made by finding rotational branches in PC-LOOMIS, and then matching differences between these branches to ground state combination differences.

The Loomis–Wood plots revealed that the upper asymmetry component of the \( F_1 \) spin component of the \( K_\sigma = 1 \) stack was perturbed by a lower energy spin component crossing above it between \( J = 37.5 \) and \( J = 38.5 \). This is the exact opposite effect to what we observed in the \( F_2 \) component of the \( K_\sigma = 0 \) stack. This was easy, because we already knew the location of these subbands to ground state combination differences. The assignment was relatively straightforward, and when we included this subband in our global fit, we determined values for the asymmetry in the rotational constants \( (B - C)/2 \) in the ground state. We then predicted the line positions for the \( K_\sigma = 1 \) stack with the \( F_3 \) component of \( F_2 \) fixed, and refit the data to obtain the spectroscopic constants listed in Table I. The fit to the individual transitions is available from PAPS, or from the authors upon request. The term values for all the spin components of \( K_\sigma = 0 \) and \( K_\sigma = 1 \) relative to those of the \( F_1 \) subband are plotted against \( J + 1/2 \) in Fig. 5(a) for the \( \tilde{X} \) state, and in Fig. 5(b) for the \( \tilde{A} \) state. The upper state plot clearly shows the interaction of the upper asymmetry \( F_1 \) component of the \( K_\sigma = 1 \) stack with the \( F_3 \) component of the \( K_\sigma = 0 \) stack. The energy of the lowest \( J \) levels for the \( F_1 \) and \( F_2 \) spin components in each \( K_\sigma \) stack is plotted for the \( \tilde{A} \) electronic state in Fig. 6. The quadratic dependence of the energy and the linear dependence of the energy splitting on \( K_\sigma \) is clearly seen in this figure.

### DISCUSSION

The \( \tilde{A} \) and \( B \) electronic states of CaSH correlate with the \( \tilde{A} \) and \( \tilde{B} \) states of CaH, and, in the "pure precession" limit, the \( \tilde{C} \) state of CaH arises from a single electron in the \( 4p \) orbital of CaH, aligned along the Ca–S bond, and the \( \tilde{A} \) and \( \tilde{B} \) states arise from a single electron in the \( 4p \) orbitals of CaH, aligned in and out of the molecular plane, respectively. In the rotating molecule, these electronic states interact by a mechanism analogous to Coriolis coupling between vibrational levels in a single electronic state. Rotation about the \( a \) axis of the molecule couples the \( \tilde{A} \) and \( \tilde{B} \) states, and induces a net orbital angular momentum into each state. This orbital angular momentum then couples with the spin of the electron to yield an effective spin–orbit parameter that depends linearly on the amount of \( a \)–axis rotation \( K_\sigma \). Whitam and Junge, in their work on the \( \tilde{A} \) and \( \tilde{B} \) states of CaH, find that the effective spin–orbit parameter depends linearly on the amount of rotation of the molecule.

### Table I. The effective spectroscopic constants of \( \tilde{X} \) and \( \tilde{A} \) states of CaSH

<table>
<thead>
<tr>
<th></th>
<th>( \tilde{X} )</th>
<th>( \tilde{A} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T )</td>
<td>0.0</td>
<td>15 380 284 67(23)</td>
</tr>
<tr>
<td>( A )</td>
<td>9.693 322(46)</td>
<td>9.090 808(78)</td>
</tr>
<tr>
<td>( (B + C)/2 )</td>
<td>0.140 722 8(33)</td>
<td>0.146 122 0(33)</td>
</tr>
<tr>
<td>( (B - C)/2 )</td>
<td>0.001 141 86(37)</td>
<td>0.001 52 8(10)</td>
</tr>
<tr>
<td>( D_N/10^{-4} )</td>
<td>8.843(16)</td>
<td>4.629(36)</td>
</tr>
<tr>
<td>( D_N/10^{-5} )</td>
<td>1.172 5(18)</td>
<td>1.993 8(28)</td>
</tr>
<tr>
<td>( D_N/10^{-7} )</td>
<td>0.953(10)</td>
<td>1.265(10)</td>
</tr>
<tr>
<td>( e_{aa})</td>
<td>-3.445 69(26)</td>
<td>0.051 676(17)</td>
</tr>
<tr>
<td>( e_{bb} )</td>
<td>0.001 388 6(69)</td>
<td>-0.026 569(29)</td>
</tr>
<tr>
<td>(</td>
<td>e_{ab}</td>
<td>/2 )</td>
</tr>
<tr>
<td>( D_N/10^{-4} )</td>
<td>-2.077(77)</td>
<td>-5.611(76)</td>
</tr>
<tr>
<td>( D_N/10^{-5} )</td>
<td>2.96(58)</td>
<td>9.090 808(78)</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>0.0040</td>
<td>9.090 808(78)</td>
</tr>
</tbody>
</table>

*Note: Values in parentheses indicate the uncertainties in the last digit.*
C. N. Jarman and P. F. Bernath: The $^2A'\leftarrow X^2A'$ transition of CaSH

transitions of CaNH$_2$ have derived formulas for the effect of this interaction on the $A$ and $e_{aa}$ spectroscopic constants derived for the $A$ and $B$ states in the pure precession limit

$$A^{\text{spec}} = A - \frac{4\lambda_\alpha^2A^2}{\Delta E_{B-A}}, \quad e_{aa} = -\frac{4\lambda_\alpha^2AA^{30}}{\Delta E_{B-A}}.$$  

Here, $A$ is the "true" value for the $a$-axis rotation constant, $\lambda$ is the component of the orbital angular momentum on the $a$ axis, $A^{30}$ is the value for the spin-orbit interaction in the parent $^1\Pi$ state, and $\Delta E_{B-A}$ is the energy difference $E(B) - E(A)$. In these formulas, the top sign refers to the $A$ state and the lower to the $B$ state.

Independent of the work reported here, Ram and Bernath have recorded some high resolution spectra of the $B^2A''\leftarrow X^2A'$ system, and a preliminary analysis of this data has yielded a band origin position at 15 860 cm$^{-1}$, and an effective spectroscopic $A$ constant of 10.14 cm$^{-1}$. This gives $A$(true) = 9.615 cm$^{-1}$ and $\Delta E$ = 480 cm$^{-1}$ for use in the above formulas, which in turn gives $\Lambda$ = 0.83 and $\Delta E = 63$ cm$^{-1}$. For a pure $^2\Pi$ parent, the value for $\Lambda$ should be unity and the fact that the formula gives a value less than this indicates that the "pure precession" approximation is not completely valid. However, the value for the spin–orbit constant $A^{30} = 63$ cm$^{-1}$ is consistent with the measured values of 71 and 66 cm$^{-1}$ for CaF and CaOH, respectively. It is interesting to perform the same calculations for CaNH$_2$ using Whitham and Jungen's data. They found that $e_{aa}$ = 8.1 cm$^{-1}$, $A$(true) = 13 cm$^{-1}$, and $\Delta E$ = 422 cm$^{-1}$, and the above formulas give $\Lambda$ = 1.0 and $A^{30}$ = 66 cm$^{-1}$. The value of $\Lambda$ = 0.83 can be rationalized by "orbital mixing" between the $^2A'$ and $^2C^2A'$ states in the nonrotating molecule. This interaction will tend to reduce $\Lambda$ from 1 in the $A$ state and increase it from zero in the $C$ state. Such an interaction is not possible in CaNH$_2$, where the $^2B_2$ and $^2C_1$ states have different symmetries.

In a similar fashion, rotation about the $b$ axis causes interactions between the $C$ and $B$ states, and rotation about the $c$ axis causes interactions between the $C$ and $A$ states. In the pure precession limit, these interactions give rise to the following values for $e_{bb}$ in the $C$ and $B$ states and $e_{cc}$ in the $C$ and $A$ states:

$$e_{bb} = \pm \frac{2l(l+1)BA^{30}}{\Delta E_{C-B}}, \quad e_{cc} = ± \frac{2l(l+1)CA^{30}}{\Delta E_{C-A}},$$

where $l$ is the electronic orbital angular momentum quantum number (1 for $p$ orbitals). In these formulas, the top sign again refers to the lower of the two states (i.e., to the $B$ state in the $e_{bb}$ formula and to the $A$ state in the $e_{cc}$ formula). In the pure precession limit, $e_{aa} = 0$ in the $C$ state, $e_{bb} = 0$ in the $A$ state, and $e_{cc} = 0$ in the $B$ state. Using $l=1$, $A^{30} = 63$ cm$^{-1}$, and $E(C) = 16 070$ cm$^{-1}$ from the observed center of the $^2C^2A'\leftarrow X^2A'$ transition in the low resolution spectrum, these formulas predict that $e_{bb} = 0$ cm$^{-1}$, and $e_{cc} = 0.053$ cm$^{-1}$, in the $A^2A'$ state compared to...
their respective experimental values of 0.025 107(34) and 0.078 245(34) cm$^{-1}$. Both experimental values are larger than the prediction by 0.025 cm$^{-1}$, but are in good qualitative agreement.

Having obtained the "true" value for the $A$ constant in the $A^2A'$ state, we used it together with the spectroscopic values for $B$ and $C$ to produce an approximate $r_0$ structure for the $A^2A'$ state. We then repeated the determination for the ground state using the spectroscopically determined value of $A''$. In each case, we constrained the geometry to be planar by calculating the geometry first with $(I_A, I_B)$ and then with $(I_A, I_C)$ pairs. We were also forced to constrain the S-H bond distance to 1.346 Å (Ref. 13) in both states. Because the molecule is an asymmetric top, no simple formulas exist for generating bond lengths and bond angles from values of $I_A$ and $I_B$, and so a nonlinear least squares fitting program was written which built up the moment of inertia tensor in terms of bond lengths and bond angles according to the formulas given in Gordy and Cook,26 diagonalized it, compared eigenvalues with the input values of $I_A$ and $I_B$, and used this difference vector to generate improved bond lengths and angles. The $r_0$ structure for both states is compared to the ab initio $r_e$ structure in Table II. The agreement for the ground state is satisfactory considering the approximate nature of both calculations. A better $r_e$ structure can only be obtained by analyzing different isotopomers of CaSH, particularly CaSD. At present, we have no plans to record these spectra.

We have also used the measured values for the spin-rotation tensor elements to calculate values for the $g$ tensor according to Curl's formula

$$g_{xx} \approx g_e - \frac{e_{ax}}{2B_x},$$

where $g_e = 2.002 32$ and $B_x$ is the rotational constant in wave numbers. The predicted values are reproduced in Table III. We hope these values will provide stimulus for others to record the electron-spin resonance (ESR) spectrum of CaSH.

**CONCLUSIONS**

We have performed the first high resolution spectroscopic analysis of the CaSH molecule, generating spectroscopic constants for the $A^2A'$ and $X^2A'$ states. CaSH is the first metal hydrosulfide to be rotationally analyzed and is an excellent example of a doublet asymmetric top with spin-rotation constants of moderate size. The $A^2A'$ state correlates with the lower energy Renner–Teller component of the $A^2T_1$ state of the isovalent molecules CaOH and CaF. An internal avoided crossing was seen between the upper asymmetry $F_1$ spin component of the $K_e=1$ stack, and the $F_2$ spin component of the $K_e=0$ stack. It seems that this type of internal perturbation is characteristic of doublet asymmetric top spectra.

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C. N. Jarman and P. F. Bernath: The $\tilde{A}^2A'\rightarrow\tilde{X}^2A'$ transition of CaSH

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