# Laser Spectroscopy of the A-X Transitions of CaOH and CaOD<sup>1</sup>

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The A-X transitions of gas phase CaOH and CaOD, produced in a low-pressure flow system, were studied by low- and high-resolution laser spectroscopy. The vibrational structure of the low-lying vibrational levels of both the A and X states were determined. A detailed rotational analysis of the (0, 0, 0)-(0, 0, 0) bands of the A-X system is presented. The spectra are well described by a  ${}^{2}\Pi$ - ${}^{2}\Sigma$  model, where the molecule is linear in both states. A preliminary analysis of the (0, 1, 0)-(0, 1, 0) bands indicates that the Renner parameter  $\epsilon$  of the  $A^{2}\Pi$  electronic state is equal to 0.073(1).

## I. INTRODUCTION

The spectrum of CaOH was first described by Herschel (1) in 1823. Herschel observed reddish and greenish emission when "muriate of lime" was added to an alcohol flame. Although the flame emission bands were definitely known to be due to a molecule containing calcium, the identification of the molecular species remained uncertain for many years. King (2) and Mahanti (3) suggested that Ca<sub>2</sub> was the emitter. Following King (4) and Lejeune and Rosen (5), Pearse and Gaydon later proposed (6) that gaseous CaO was the emitter. However, in 1955, by noting similarities and systematic changes in the alkaline-earth halide diatomic molecule emission spectra, James and Sugden (7) suggested that the observed bands were due to calcium monohydroxide. Similar bands observed with strontium and barium flames were supposedly due to the corresponding monohydroxides.

The similarities among the alkaline-earth halide spectra are explained by noting that the observed optical bands are due to transitions between electron orbitals localized near the metal-atom end of the molecule (8). The lowest-energy electronic transitions then involve the promotion of a nonbonding electron in an  $ns\sigma(X)$  orbital located primarily on the metal to a metal  $np\pi(A)$  or metal  $np\sigma(B)$  orbital. Since the transitions are localized on the metal ion, the molecular structures and potential curves of the electronic states are very nearly the same. Hence, due to the Franck-Condon factors, the spectrum consists of very strong  $\Delta v = 0$  sequences, which are badly overlapped. Since CaOH is isoelectronic with CaF, their optical spectra are expected to be similar.

Further confirmation of the assignment of these bands came from the substitution

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of  $D_2O$  for  $H_2O$  in flames (9) and arcs (10). Although a clear isotope effect was observed for strontium bands, no significant shift was seen for calcium. Huldt and Lagerqvist (11) reinvestigated the Sr and Ca arc and flame spectra to search for isotope effects and to identify clearly the source of the bands. An isotope effect was seen in the "orange" system of strontium, but none in the red system (670–690 nm). They found no isotope effect in either the yellow green (540–570 nm) region or the red region (600–630 nm) of calcium.

Van der Hurk, Hollander, and Alkenade (12, 13) made careful and systematic observations of Ca in air-acetylene flames and identified the wavelengths of small, but reproducible peaks in the emission. Other work by Human and Zeegers (14) showed that the flame emission bands and white-light-induced fluorescence bands, purportedly due to CaCH in a hydrogen-oxygen flame, were identical. In 1978, a tunable dye laser was used (15) to observe excitation and fluorescence spectra of CaOH in an air-acetylene flame. However, the laser-induced spectra in this high-temperature flame were essentially identical to the flame emission bands. A tentative, diatomic-like vibrational analysis was suggested (15).

In summary, we see that in spite of nearly 150 years of spectroscopic effort, the identification of CaOH as the dominant molecular emitter in these calcium-containing flames had not been unambiguously established. Moreover, the structure of the molecule (linear or bent) and its spectroscopic constants remained unknown.

In Section II, we describe a method of production of CaOH and CaOD in a lowtemperature, low-pressure flow system. Section III contains a description of low resolution dye laser spectroscopy of CaOH and CaOD, which establishes the identity, structure, and vibrational analysis of these molecules. Details of the high-resolution dye laser spectroscopy and rotational analysis of the (0, 0, 0)–(0, 0, 0) vibrational band of the  $A^2\Pi-X^2\Sigma$  electronic bands of both CaOH and CaOD are presented in Section IV. In Section V is found a brief discussion of the results of the rotational analysis. A preliminary analysis of the Renner–Teller effect in the (0, 1, 0)–(0, 1, 0) bands of the A-X transitions of CaOH and CaOD is given in Section VI. Finally, some concluding remarks are made in Section VII.

# II. PRODUCTION OF CaOH AND CaOD

The summary of previous work on CaOH and CaOD given in the Introduction indicates that high-temperature flames do not provide a hospitable environment for high-resolution spectroscopy of these molecules. Over the past decade, extensive high-resolution spectroscopy of the alkaline-earth halides and oxides and other diatomic molecules has been carried out in low-pressure, flowing gas-phase reaction systems (16). Recently, it has been shown (17) that abundant quantities of polyatomic molecules can also be produced in this type of system. High-resolution laser spectroscopy of the *B*-X system of SrOH and SrOD (18) and the  $\tilde{C}^2A_1-\tilde{X}^2A_1$  system of CaNH<sub>2</sub> (19) has shown that the molecules produced in the flow system are quickly equilibrated with the cool, low-density carrier gas, and thus provide an ideal sample for spectroscopic studies.

Although the details of the flow system have been provided previously (16, 17), for completeness' sake, we summarize the method of production of CaOH and



FIG. 1. Block diagram of the experimental equipment. "PM" indicates a photomultiplier tube. "L" indicates a lens.

CaOD. Calcium atoms entrained in a low-pressure flow of argon react with water vapor (or heavy water vapor) to produce CaOH (or CaOD). The calcium atoms are vaporized from an alumina crucible heated with a tungsten resistance wire heater. A flow of a few tenths mmol/sec of argon entrains the metal atoms and carries them a few centimeters to a reaction region where water vapor is present. The system pressure is typically a few Torr. The water vapor partial pressure is a few milliTorr. This reaction produces easily visible chemiluminescence (17). The observed chemiluminescence spectrum is quite broad and is similar in structure to the bands observed in high-temperature, calcium-containing flames.

## III. VIBRATIONAL SPECTROSCOPY

Low-resolution photoexcitation spectra were observed near 625 and 600 nm by directing the beam of a cw tunable dye laser (Spectra-Physics Model 580) into the reaction zone described in Section II. The dye laser was run multimode and had an effective bandwidth of about 0.01 nm. Figure 1 shows a block diagram of the experimental apparatus. The total undispersed photoluminescence was observed with an RCA 4832 photomultiplier tube, whose spectral response is essentially flat between 400 and 800 nm. The laser beam was chopped at a frequency of about 700 Hz. Synchronous detection of the ac component of the photomultiplier tube current discriminated against the chemiluminescence emission. A ground-state vibrational analysis was carried out by fixing the laser wavelength and spectrally analyzing the laser-induced photoluminescence emission with a 1.0-m focal length monochromator.

Figure 2 displays the total undispersed photoluminescence signal observed for CaOH as a function of the excitation laser wavelength near 625 nm. The laser wavelength was determined with an uncertainty of about 0.01 nm by the 1.0-m monochromator. These moderate-resolution laser excitation spectra are useful in determining the overall structure of the spectra and serve as a guide for the analysis of the high-resolution spectra described below. Portions of the CaOH and CaOD spectra are compared in Fig. 3. Somewhat weaker excitation spectra were observed near 600 nm and are displayed in Fig. 4.



FIG. 2. Low-resolution photoexcitation spectrum of CaOH. The wavelength markers on the abscissa are only approximate due to nonlinearities in the laser wavelength scanning drive.

Since the spectra shown in Figs. 2-4 are similar in structure to those observed for CaF (20-24), we are led directly to the following analysis: The excitation spectrum near 625 nm is a  $\Delta v_i = 0$  (i = 1, 2, 3) sequence of *P*-branch (violet-degraded) bandheads belonging to the *A*-X electronic transitions of CaOH and CaOD. The spectrum observed near 600 nm is assigned to the  $\Delta v_1 = +1$  sequence. The two subgroups of bandheads seen in Figs. 2 and 4 are due to the spin-orbit splitting in the excited  $A^2\Pi$  state. The separation between corresponding bandheads in the two



FIG. 3. Comparison of portions of the CaOH and CaOD photoexcitation spectra.



FIG. 4. CaOH an CaOD photoexcitation spectra near 602 nm.

subgroups yields an estimate of 67(1) cm<sup>-1</sup> for the spin-orbit splitting constant of the A state. (The spin-orbit splitting constant in the  $A^2\Pi$  state of CaF is about 71 cm<sup>-1</sup>.) These spectra are the first to show the spin-orbit splitting for an alkalineearth monohydroxide molecule. We conclude that CaOH and CaOD are linear molecules, a conclusion justified in detail by the rotational analysis presented below.

The formation of the *P*-branch heads indicates that the rotational constant of the excited state is greater than that of the lower state. We also expect to find the excited-state vibrational constants  $\omega'_i$  greater than those of the lower state. Thus, we tentatively recognize the successive bandheads proceeding to the blue as members of a  $\Delta v_i = 0$  sequence with  $(v_1, v_2, v_3) = (0, 0, 0), (0, 1, 0), (1, 0, 0)$ , etc. As usual,  $v_1$  denotes the vibrational quantum number of the mode associated with the Ca-O stretch;  $v_2$  is the bending mode vibrational quantum number, and  $v_3$  is the quantum number of the mode associated with the Ca-O stretch;  $v_2$  is the bending mode vibrational quantum number, and  $v_3$  is the quantum number of the CaOH spectra are quite similar to the CaOH spectra but have a slight (about 0.1 nm) overall red shift. Also, the CaOD spectra show a more pronounced "filling in," as one would expect since the bending vibration frequency and rotation constants of CaOD are smaller than those of CaOH.



FIG. 5. The spectrum of the photoluminescence of CaOD with the laser excitation wavelength fixed at 623.85 nm. The spectrometer resolution was about 0.1 nm.



FIG. 6. The vibrational structure of CaOH  $X^2\Sigma$  as determined by measurement of the photoluminescence spectra. The levels indicated by solid lines were pumped directly in observed transitions. The positions of levels indicated by dashed lines are calculated. The position of the (0, 1, 0) level relative to the (0, 0, 0) level was calculated. The uncertainty in the level spacings is about 1 cm<sup>-1</sup>.

By fixing the excitation wavelength at one of the  $\Delta v_i = 0$  bandheads and measuring the spectrum of the photoluminescence, we have determined the ground-state vibrational structure directly. A typical photoluminescence spectrum is shown in Fig. 5. Note that the intensity of the  $\Delta v_1 = -1$  emission is only a few percent of the intensity of the  $\Delta v_1 = 0$  emission. The rapidly decreasing Franck-Condon factor with increasing  $\Delta v_1$  is symptomatic of the nonbonding character of the orbitals involved in these electronic transitions.

Figures 6 and 7 show the vibrational structures determined from the photoluminescence spectra in CaOH and CaOD. The levels were assigned by a combination of self-consistency checks, relative intensities based on appropriate Boltzmann factors for the assigned levels, and the relative positions of the excitation within the



FIG. 7. The vibrational structure of CaOD  $X^2\Sigma$  as determined by measurement of the photoluminescence spectra. See the caption of Fig. 6 for additional comments.

x <sup>2</sup> Σ	CaOH	CaOD
ω <sub>1</sub> + ½ × <sub>13</sub>	622.6(10)	613.6(10)
×11	-3.1(10)	-2.6(10)
* <sub>12</sub>	-10.3(20)	-5.3(10)
$2\omega_2 + 12x_{22} + x_{23}$	689.0(20)	492.0(40)
а <sup>2</sup> П		
ω <sub>1</sub> + ½ x <sub>13</sub>	634.7(20)	623.3(20)
$2\omega_2 + 12x_{22} + x_{23}$	702.0(40)	497.0(40)

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Vibrational Constants (in cm<sup>-1</sup>) for CaOH and CaOD

Note. The figures in parentheses are the uncertainties in the last digit.

 $\Delta v_i = 0$  sequence (assuming  $\omega'_i > \omega''_i$ ). For example, when molecules are excited from the (0, 0, 0) and (0, 1, 0) of the ground state, no short wavelength emission (corresponding to  $\Delta v_1 = +1$  or  $\Delta v_2 = +2$ ) should be or is observed. An uncertainty of about 0.5 cm<sup>-1</sup> in the level spacings arises from the spectrometer resolution and another (conservative) 0.5 cm<sup>-1</sup> from the spectrometer calibration. Thus, a conservative 1 cm<sup>-1</sup> uncertainty is assigned to the energy difference given.

In the photoluminescence spectrum of CaOH, we observed emission from  $A^2\Pi(0, 1, 0)$  to  $X^2\Sigma(0, 3^1, 0)$  corresponding to  $\Delta v_2 = -2$  for the bending vibration mode. This emission has an intensity about  $10^{-3}$  of the intensity of the  $\Delta v_2 = 0$  emission. Selection rules for the bending mode transitions (25) are  $\Delta l_2 = 0$  and hence,  $\Delta v_2 = 0, \pm 2, \pm 4$ , etc., since the vibrational angular momentum quantum number  $l_2$  can take on the values  $l_2 = v_2, v_2 - 2, \ldots, 1$  or 0. Since the equilibrium position for the bending vibrations in the upper state is directly "over" the equilibrium position in the lower state (viz., at  $r_2 = 0$ , the linear configuration) and since  $\omega'_2 \simeq \omega''_2$ , we expect only the  $\Delta v_2 = 0$  sequence to have significant oscillator strength. For CaOD, the  $\Delta v_2 = 0$  emission intensity. We believe that the CaOH  $\Delta v_2 = -2$  emission has significantly higher strength because of a Fermi resonance between the  $X^2\Sigma(1, 1, 0)$  and  $(0, 3^1, 0)$  states. Fermi resonances are also responsible, we believe, for the complex structure observed in the CaOH, but not in the CaOD, spectra shown in Fig. 4.

The vibrational structure of a linear XYZ molecule can be described by the term formula (25)

$$T_{ev} = T_e + G(v_1 v_2^{l_2} v_3), \tag{1}$$

where

$$G(v_1v_2'v_3) = \sum_i (v_i + d_i/2)\omega_i + g_{22}l_2^2 + \sum_{i < j} (v_i + d_i/2)(v_j + d_j/2)x_{ij}.$$
 (2)

Here  $d_i$  is the degeneracy factor for the *i*th mode:  $d_1 = d_3 = 1$ ;  $d_2 = 2$ ;  $\omega_i$  is the (harmonic) frequency for the *i*th mode. The anharmonicity constants are the  $x_{ij}$ . Symmetry requires that  $x_{ij} = x_{ij}$ ;  $g_{22}$  gives the splitting of levels with the same  $v_2$ 

but different values of the vibrational angular momentum quantum number  $l_2$ . Table I lists the vibrational constants for the ground state determined from the energy level structure given in Figs. 6 and 7. Since we have observed only a few level spacings, none of which involve the CaO-H stretching mode, we can determine only the combinations of terms listed in Table I.

Approximate vibrational constants for the  $A^2\Pi$  states can be found from the  $\Delta v_1 = +1$  photoexcitation spectra shown in Fig. 4 and also from the ground-state constants and a knowledge of the separation of the  $\Delta v_i = 0$  sequence bandheads. These excited-state constants are given in the lower part of Table I.

One can use the relative intensities and the vibrational constants determined above to estimate a vibrational temperature for the molecules excited by the laser. Although this temperature carries considerable uncertainty due to the overlapping of bands as the laser proceeds from the red to the blue in each subgroup, the estimated temperature of  $700 \pm 50$  K indicates considerable relaxation of the calcium monohydroxide molecules in the argon carrier gas. This temperature is consistent with the translational temperature determined by single-mode laser scans described in Section IV.

## IV. HIGH-RESOLUTION ROTATIONAL SPECTROSCOPY

By replacing the multimode laser with a single-mode ring dye laser (Spectra-Physics Model 380A), we carried out a high-resolution rotational analysis of CaOH and CaOD. In order to tune the ring laser over several cm<sup>-1</sup> in a single scan, we removed the rotating "galvanometer plate" (a rotating solid quartz plate, which varies the optical path length of the laser cavity). When the air-spaced etalon of the laser cavity is piezoelectrically tuned, the laser output frequency then jumps from one cavity mode to the next. Since the cavity mode spacing (200 MHz) is much less than the Doppler width (about 1 GHz) of the observed lines in CaOH and CaOD, the stepped nature of the scan has negligible effect on the observed spectra. Using an intracavity etalon with a free-spectral range of 75 GHz, we were able to achieve scan lengths of about 70 GHz with essentially constant laser output power. (Use of the rotatable plate allows continuous scanning of the laser output, but results in significant (±30%) power variations during a 30-GHz scan). An auxiliary (extracavity) Fabry-Perot interferometer monitored the laser output to verify single-mode operation and smooth scanning. In this manner overlapping scans covering about 150 cm<sup>-1</sup> near 625 nm were carried out for both CaOH and CaOD.

The laser output frequency was determined by recording simultaneously the CaOH (or CaOD) photoluminescence and the photoluminescence of molecular  $I_2$  excited by part of the same laser beam. Wavenumbers of the observed  $I_2$  lines were taken from the tabulation of Gerstenkorn and Luc (26). CaOH and CaOD line positions were determined with an uncertainty of 0.01 cm<sup>-1</sup>.

Using the vibrational analysis of Section III and the relative intensities of the observed lines made the identification of lines belonging to the (0, 0, 0)-(0, 0, 0) band straightforward.

Figure 8 shows a 1.2-cm<sup>-1</sup> section of a photoexcitation scan near one of the bandheads of CaOH. The 200-MHz steps of the laser scan are just visible in that



FIG. 8. High-resolution, single-mode laser excitation spectrum of CaOH near the  $P_1 + Q_{12}$  bandhead. The lower trace is the photoexcitation spectrum of molecular iodine, recorded simultaneously. The numbers on the abscissa are the line numbers in the catalog of Ref. (26). The small steps in the spectra are due to the 200-MHz mode jumps of the laser.

figure. The lower trace in Fig. 8 shows the  $I_2$  photoexcitation signal recorded simultaneously. The numbers on the lower horizontal axis are the catalog numbers of Ref. (26).

The Doppler width of the individual spectral lines was determined to be 1.2(2) GHz (full width at half-maximum). From this measured width, a translational temperature of  $700 \pm 140$  K was found for CaOH and CaOD. This translational temperature is consistent with the vibrational temperature estimated in Section III.

The (0, 0, 0)- $(0, 0, 0)^2\Pi$ - $\Sigma^+$  band of a linear (triatomic) molecule should be identical in structure to a  ${}^{2}\Pi$ - ${}^{2}\Sigma^+$  band of a diatomic molecule (25, 27). Hence, we expect to find for a good Hund's case (a) molecule (with  $A \ge B$ ), twelve rotational branches split into two subbands by the spin-orbit interaction. The two subbands originate from the  $A^2\Pi_{3/2}$  and  $A^2\Pi_{1/2}$  states, with the  $\Omega = 3/2$  levels lying above the  $\Omega = 1/2$  levels for a regular  ${}^{2}\Pi$  state.

Originating from the  ${}^{2}\Pi_{3/2}$  levels are the branches  $R_2$ ,  $R_{21}$ ,  $P_2$ ,  $P_{21}$ ,  $Q_2$ , and  $Q_{21}$ , where the subscripts refer to the  $F_1$  or  $F_2$  levels involved in the transition (27). (An  $F_1$  level has J = N + 1/2; and  $F_2$  level has J = N - 1/2.) When the spin splitting in the  ${}^{2}\Sigma^{+}$  state is very small (as it is for CaOH, CaOD, and CaF), then the  $P_{21}$  and  $Q_2$  branches coincide, and the  $R_2$  and  $Q_{21}$  branches coincide. Thus, only four distinct branches are observed in each subgroup. In CaOH and CaOD, the  $P_{21}$  and  $Q_2$ branches form a bandhead. Originating from the  ${}^{2}\Pi_{1/2}$  levels, the branches  $R_{12}$  and  $Q_1$  coincide and the  $P_1$  and  $Q_{12}$  branches coincide. The  $P_1$  and  $Q_{12}$  branches form a bandhead.

By fixing the laser wavelength at the peak of a rotational line and measuring the photoluminescence spectrum with the 1.0-m monochromator, we assigned angular

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#### TABLE II

Observed Line Positions (in cm <sup>-1</sup>	) and Angular Momentum Quantum	Number Assignments of the
(000)-(000	) Bands of $A^2\Pi - X^2\Sigma$ for CaOH and C	CaOD

J	R <sub>2</sub> (J) Frequency	Diff.	J	Q <sub>2</sub> (J) Frequency	Diff.
			2.5	16 029.933	-0.005
			3.5	029.661	-0.009
			4.5	029.383	0.015
			5.5	029.156	0.009
6.5	16 034.075	0.002	6.5	028.927	0.010
7.5	034.542	-0.001	7.5	028.744	0.011
8.5	035.033	-0.005	8.5	028.547	-0.013
9.5	035.564	0.002	9.5	028.373	-0.003
10.5	036.089	0.010	10.5	028.217	-0.003
11.5	036.629	-0.011	11.5	028.052	-0.015
12.5	037.197	-0.000	12.5	027.939	-0.024
13.5	037.783	0.007			
14.5	038,356	0.018			
12.2	038.978	0.008			
17.5	039.613	0.020			
1/.5	040.208	0.011		Dand No.	
10.5	040.913	0.012		Dalia nea	20
20.5	041.000	0.012			
21 5	043.010	0.010			
22.5	043.731	-0.003			
23.5	044.474	0.000			
24.5	045.232	-0.020			
			<b>26</b> F	10 007 000	
			26.5	10 02/.966	-0.007
			27.5	028.082	-0.001
			28.5	028.21/	0.010
			29.5	028,395	-0.014
			31 5	028.3783	-0.010
			32.5	020.705	-0.001
			33 5	020.370	-0.021
			34.5	029.453	0.000
			35.5	029.694	-0.013
			36.5	029.986	0.009
			37.5	030,285	0.006
			38.5	030.582	0.014
			39.5	030.930	0.005
			40.5	031.269	0.004
			41.5	031.636	0.004
			42.5	032.003	0.002

(000) - (000) Band of CaOH

Note. "Diff." is the difference between the observed line position and the line position calculated using Eqs. (3)-(7) and the parameters determined by the least-squares analysis.

momentum quantum numbers to the observed lines with the P-R separation method (20). About 80 lines belonging to the (0, 0, 0)-(0, 0, 0) branches were assigned directly in this manner. Other lines, which obviously were members of a rotational branch, were assigned simply by counting from the directly assigned lines. The assigned quantum numbers and measured frequencies of 131 rotational lines belonging to the  $R_2 + Q_{21}, P_{21} + Q_2, R_{12} + Q_1, P_1 + Q_{12}, and P_{12}$  branches of the (0, 0, 0)-(0, 0, 0) band of CaOH are listed in Table II. Also listed in that table are the J values and observed frequencies for 41 lines of the  $Q_1$  and  $P_1$  branches of CaOD.

The  $R_{21}$  lines occur in the same spectral region as the stronger  $R_2$  and  $Q_{21}$  lines. Similarly, the  $R_1$  lines are found among the stronger  $Q_1$  and  $R_{12}$  lines. Since the molecular constants are already overdetermined by the assigned lines, no effort was made to assign  $R_{21}$  and  $R_1$  lines.

For a good case (a) molecule, the energy levels of a <sup>2</sup>II state are described by the formulae (27, 28)

$$F_{ic}(J) = T_v - A_v/2 + B'_v(1/2)J(J+1) - D'_v(1/2)J^2(J+1)^2 - (p_v/2)(J+1/2), \quad (3)$$

$$F_{1d}(J) = T_v - A_v/2 + B'_v(1/2)J(J+1) - D'_v(1/2)J^2(J+1)^2 + (p_v/2)(J+1/2), \quad (4)$$

$$F_{2c} = F_{2d} = T_v + A_v/2 + B'_v(3/2)J(J+1) - D'_v(3/2)J^2(J+1)^2.$$
(5)

## TABLE II-Continued

 $P_1(J)$  $Q_1(J)$  $P_{12}(J)$ Diff. J Frequency Diff. .1 Frequency Diff. J Frequency 2.5 15 964.091 0.013 3.5 0.008 963.811 963.551 0.002 -0.000 5.5 963.290 6.5 963.030 0.011 7.5 962.780 0.007 8.5 962.544 -0.007 8.5 15 967.952 -0.000 968.364 0.005 9.5 962.332 0.007 9.5 15 954.326 0.006 968.785 -0.007 10.5 10.5 962.116 0.008 10.5 11.5 961.900 -0.010 11.5 969.217 -0.013 11.5 953.424 -0.007 12.5 969.665 -0.002 12.5 952.525 0.008 961.723 -0.000 12.5 13.5 961.544 -0.010 13.5 970.109 0.006 13.5 951.630 -0.013 961.356 970.569 0.008 950.737 -0.003 -0.005 14.5 14.5 949.884 -0.021 15.5 961.207 0.001 15.5 971.056 -0.012 15.5 961.049 -0.004 16.5 971.550 -0.013 16,5 949.005 0.020 16.5 17.5 17.5 972.050 -0.008 17.5 948.168 0.011 960.917 -0.003 960.797 0.007 18.5 972.538 -0.008 18.5 947.314 0.002 18.5 19.5 973.056 0.013 19.5 946.530 0.002 19.5 960.677 0.010 945.707 -0.005 20.5 973.590 0.007 20.5 21.5 974.130 -0.008 21.5 944.895 -0.006 22.5 974.702 -0.009 22.5 944.104 -0.006 23.5 975.258 23.5 943.317 -0.004 -0.011 24.5 975.815 -0.005 24.5 942.547 0.005 976.397 941.789 0.004 -0.001 25.5 25.5 26.5 976.990 0.007 26.5 941.045 -0.000 27.5 977.600 -0.002 27.5 940.319 0.006 28.5 978.220 -0.007 28.5 939.594 0.006 978.855 29.5 938.878 0.002 29.5 -0.011 938.183 979.484 0.009 30.5 0.003 30.5 31.5 980.127 0.001 31.5 937.495 0.003 980.783 0.007 32.5 936.813 0.004 32.5 33.5 981.473 -0.015 33.5 936.149 -0.006 34.5 0.003 982.147 -0.008 935.495 34.5 0.006 35.5 982.846 0.008 35.5 934.853 36.5 934.213 0.003 37.5 933.604 0.011 38.5 933.000 0.010 39.5 932.403 0.001 40.5 -0.000 931.828 -0.004 41.5 931.257 -0.016 42.5 930.690 43.5 930.143 -0.000 44.5 929,606 -0.002 45.5 929.073 0.000 46.5 928.580 0.000 47.5 928.082 0.000

(000) - (000) Band of CaOH

		(000) ·	- (000) B	and of	CaOD	
J	Q <sub>1</sub> (J) Frequency	Diff.		J	P <sub>1</sub> (J) Frequency	Diff.
				4.5	15 960.564	-0.021
				5.5	960.345	0.002
	15 054 004			6.5	960.123	0.013
7.5	15 964.224	0.008		7.5	959.879	-0.007
8.5	964.588	0.009		8.5	959.6/0	-0.003
9.5	964.967	0.016		9.5	959.4/0	0.002
10.5	902.339	0.000		10.5	939.279	0.005
11.5	965.705	~0.019				
13.5	966 526	~0.007				
14.5	966.955	0.007				
15.5	967,393	0.012				
16.5	967,809	-0.009				
17.5	968,263	-0.002				
18.5	968.735	0.013				
19.5	969.185	-0.003				
20.5	969.654	-0.010				
21.5	970.158	0.009				
22.5	970.647	0.003				
23.5	971.142	-0,006				
24.5	971.657	-0.005				
25.5	972.206	0.020				
26.5	972.710	-0.009				
27.5	973.258	-0.004				
28.5	973.802	-0.013				
29.5	974.376	-0.002				
30.5	974.936	-0.014				
31.5	975.524	-0.009				
32.5	970.141	0.010				
33.3	9/0./41	0.013				
34.3	977 969	0.003				
36.5	978.604	0.007				
37,5	979,250	0.010				
38.5	979,899	0.005				
39.5	980.543	-0.015				
40.5	981.227	-0.005				······

TABLE II-Continued

For a case (b)  $^{2}\Sigma$  state, the energy levels are given by

$$F_1(N) = B_v'' N(N+1) - D_v'' N^2 (N+1)^2 + (\gamma_v/2)N,$$
(6)

$$F_2(N) = B_v'' N(N+1) - D_v'' N^2 (N+1)^2 - (\gamma_v/2)(N+1), \tag{7}$$

where the symbols have their usual spectroscopic meanings. All hyperfine interaction terms have been neglected.<sup>4</sup>

The values of the spectroscopic parameters were determined by a weighted, linear least-squares fit of the observed wavenumbers listed in Table II to the wavenumbers calculated using Eqs. (3)-(7). The expected splitting of the observed lines due to the spin interaction in the  $X^2\Sigma$  state was observed for only a few high J lines in the  $R_2 + Q_{21}$  branches of CaOH. Unfavorable intensity ratios (29) preclude observing the splitting in the  $Q_2 + P_{21}$  and  $Q_1 + R_{12}$  branches. The  $Q_{12} + P_1$  branches should

<sup>&</sup>lt;sup>4</sup> The hyperfine structure of the X state of CaF has been recently measured (Ref. (22-24)). Based on those measurements, estimates of the hyperfine structure of CaOH and CaOD indicate that the hyperfine structure is far smaller than the linewidth observed in the work reported here.

show the sign splitting for sufficiently high J values, but those high J lines occur in a complex bandhead region. Since the observed splittings allowed only an approximate determination of the spin constant  $\gamma_0$ , the value of  $\gamma_0$  was fixed for the leastsquares fit at the value determined for the CaF  $X^2\Sigma$  state, namely,  $\gamma_0 = 0.0013$ cm<sup>-1</sup>. That value is consistent with the few splittings observed in CaOH.

Since relatively few lines were assigned for CaOD, it was necessary to fix the value of the  $\Lambda$ -doubling constant  $p_v$  to obtain a stable least-squares fit (i.e., a fit independent of the initial assumed values of the parameters). A value for  $p_v$  was calculated using the "unique perturber" model of Zare (see Section V) and the well-determined value of  $p_v$  for CaOH.

Table II lists the differences between the observed and calculated line positions. The standard deviation for the line positions is  $0.009 \text{ cm}^{-1}$  for CaOH and  $0.011 \text{ cm}^{-1}$  for CaOD. These results are consistent with the estimated measurement uncertainties stated above. The values of the parameters and their associated 95% confidence uncertainties determined by the least-squares fit are listed in Table III.

#### V. DISCUSSION

As expected for a good case (a) molecule, the observed spectra for CaOH and CaOD are well described by a fit to the expressions given in Eqs. (3)-(7). Thus, there

## TABLE III

Spectroscopic Parameters (in cm<sup>-1</sup>) for CaOH and CaOD. The Numbers in Parentheses are the 95% Confidence Limit Uncertainties Determined by the Least-Squares Analysis

	Α <sup>2</sup> Π (000	))
	Caoh	CaOD
T	15997.8715(3)	a
A	66.1508(5)	a
B <sub>0</sub> (1/2)	0.339796(8)	0.30828(8)
B <sub>o</sub> (3/2)	0.342900(8)	a
D <sub>0</sub> (1/2)	3.91(5) x 10 <sup>-7</sup>	1.1(5) x 10 <sup>-0</sup>
D <sub>o</sub> (3/2)	$4.68(5) \times 10^{-7}$	a
р	-0.04371(3)	-0.0397 <sup>c</sup>
	x <sup>2</sup> Σ (000	))
Bo	0.334506(8)	0.30359(8)
Do	4.39(5) x 10 <sup>-7</sup>	1.2(5) x 10
Y.	0.0013 <sup>b</sup>	0.0013 <sup>b</sup>

a. Not determined.

b. Estimated. See text for details.

c. Calculated. See text for details.

Bond Lengths in CaOH and CaOD (in Angstroms)

O A	x <sup>2</sup> Σ	а <sup>2</sup> П
r <sub>o</sub> (Ca-0)	1.986	1.966
r <sub>e</sub> (Ca-0)	1.976(4)	1.956(4)
r <sub>0</sub> (0-H)	0.901	0+897
r <sub>e</sub> (O-H)	0.930(7)	0.923(7)

The uncertainties in parentheses are determined by the estimated uncertainties in the vibrational corrections to the rotational constants.

is no doubt that CaOH and CaOD are linear in both the X and A states. The effective B values in Eqs. (3)-(5) may be combined to find the "true" rotation constant (30) for the  $A^2$ II state of CaOH:

$$B'_0 = [B'_0(1/2) + B'_0(3/2)]/2.$$
(8)

We find that  $B'_0(CaOH) = 0.341348(11) \text{ cm}^{-1}$ .

Since the rotation constants are known for both CaOH and CaOD, the Ca–O and O–H bond lengths may be determined if it is assumed that the bond lengths are the same in both molecules. However, since the rotation constants have been determined only for the (0, 0, 0) vibration states, we must estimate the vibrational corrections to the rotation constants to find the equilibrium rotation constants and the equilibrium bond lengths. The equilibrium values are related to the measured values by the expression (25)

$$B_e = B_v + \sum_i \alpha_i (v_i + d_i/2), \qquad i = 1, 2, 3.$$
(9)

Here  $\alpha_i$  is the vibrational correction for the *i*th vibrational mode. To determine approximate  $B_e$  values, we let  $\alpha_1 = 2.4 \times 10^{-3}$  cm<sup>-1</sup>, which is the  $\alpha$  value for CaF (21). The value of  $\alpha_2$  for CaOH and for CaOD may be estimated from the measured values for SrOH and SrOD (18). We may use the estimate of  $\alpha_3$  determined by Lide and Matsumura (31) for CsOH and RbOH to estimate a value of  $\alpha_3$  for CaOH and CaOD. Using these values for both the X and A states, we find the equilibrium bond lengths listed in Table IV, where the uncertainty in the  $r_e$  values is due entirely to the estimated uncertainties in the  $\alpha$  values. For comparison, we have listed bond lengths and vibrational frequencies for several similar molecules in Table V. Although the uncertainties in the  $r_e$  values are large, some general trends may be noted: (1) The  $r_0(O-H)$  bond length is considerably shorter than the  $r_e$  value. This shorter bond length can be understood as the effective projection of the O-H bond length along the molecular "a" axis during the large amplitude zero-point bending motion. (2) Since the Ca-O bond length decreases in going from the X to the A state, we conclude that the "nonbonding" valence electron is actually slightly antibonding. (3) The Ca-O bond length is slightly larger than the interatomic distance in CaF,

but shorter than that in CaO. The O-H bond length in CaOH is somewhat shorter than that in the OH radical. Similar relations have been found for the bond lengths of SrOH and SrOD (18).

The  $\Lambda$ -doubling constant for CaOH can be calculated by the following expression using the Van Vleck "pure precession" model (25) and the Zare "unique perturber" model (30):

$$p = 2A_{\Pi}B_{\Pi}L(L+1)/E(A^{2}\Pi) - E(B^{2}\Sigma).$$
(10)

Assuming that L = 1 for an unfilled  $\pi$  orbital (a  $p\pi$  orbital centered on Ca) and that E(A) - E(B) = -2053 cm<sup>-1</sup> (as determined by the chemiluminescence spectrum), we find that p = -0.0439 cm<sup>-1</sup>. This value is in excellent agreement with the measured value listed in Table III. Using the ratio of the measured rotation constants for CaOH and CaOD, we may then calculate that p(CaOD) = -0.039 cm<sup>-1</sup>. Since we did not have sufficient data to determine p(CaOD) uniquely from the least-squares fit, the value of p(CaOD) was fixed at the value given above.

The expected relationship among the centrifugal distortion constant D, the rotation constant, and the vibrational frequencies is more complicated in linear polyatomics than it is in diatomics. Nielsen (32) has shown that for an XYZ linear molecule, D can be expressed as

$$D = 4B^{3}(\delta_{1}/\omega_{1}^{2} + \delta_{3}/\omega_{3}^{2}), \qquad (11)$$

where  $\delta_1$  and  $\delta_3$  are constants, which for CaOH and CaOD are on the order of unity. Using  $\delta_1 = \delta_3 = 1$ ,  $\omega_3 = 3700 \text{ cm}^{-1}$ , and the measured values for *B* and  $\omega_1$ , we find that the expression above yields  $D = 4.1 \times 10^{-7} \text{ cm}^{-1}$  for CaOH, which is in reasonable agreement with the values given in Table III. The *D* values determined by the least-squares fit for CaOD are larger than the values calculated from Eq. (11), but the uncertainties in the measured values are large because of the paucity of data for high *J* lines in CaOD.

## VI. RENNER-TELLER EFFECT

When the bending vibration mode is excited  $(v_2 \neq 0)$ , additional level splittings arise because of the breaking of the linear  $(C_{\infty})$  symmetry of the molecule. In par-

## TABLE V

Bond Lengths (in Angstroms) and Vibrational Frequencies (in cm<sup>-1</sup>) for CaOH and Similar Molecules

	CaOH <sup>a</sup>	КОН	CaF <sup>d</sup>	Ca0 <sup>e</sup>	OH
r <sub>e</sub> (M-0)	1.976(4)	2.2115 <sup>b</sup>	1.967	1.8221	****
r <sub>e</sub> (0-H)	0.930(7)	0•9120 <sup>b</sup>		*****	0.9697
ω <sub>1</sub> (M-O)	606(1)	408 <sup>°</sup>	586.0	728.7	**
ω <sub>2</sub> (M-O-H)	339(1)	300 <sup>¢</sup>	-90 W -20 W	<del>تە تە تە تە</del>	inte suit muy dan
ω <sub>3</sub> (0-H)	x	x	-and they are and	الله فله تبت هو	36953.4



FIG. 9. Sketch of the Renner-Teller splitting of the (010) levels of a  ${}^{2}\Pi$  (electronic) state. The notation is that used in Ref. (36).

ticular, in the  $A^2\Pi$  excited state, the interaction of the electronic orbital angular momentum with the vibrational angular momentum should lead to, via the Renner-Teller effect (25, 33, 34), a substantial splitting of the observed levels. The rotational structure of a  ${}^{2}\Pi$  electronic state of a linear triatomic molecule in the presence of an excited bending mode has been treated in detail by Hougen (35). Since our analysis of the (0, 1, 0)-(0, 1, 0) A-X transitions is not extensive, we will simply quote appropriate results to justify the preliminary conclusions.

When the spin-orbit splitting of the molecule is large compared to the Renner-Teller splitting, the vibronic levels of the (010) state of a <sup>2</sup>II electronic state occur as shown in Fig. 9. The rotational structure of the <sup>2</sup> $\Sigma$  vibronic levels is similar to the rotational structure of a case (a) <sup>2</sup>II<sub>1/2</sub> state or a case (c)  $\Omega = 1/2$  state if A is very much larger than both the Renner-Teller splitting (which is roughly  $(\epsilon \omega_2)^2/A$ ) and BJ (see Eq. (25) of Ref. (35)) with effective rotation constants which depend on the spin-orbit parameter A and the Renner-Teller parameter  $\epsilon \omega_2$  much as the effective rotation constants in a case (a) diatomic molecule depend on A. The primary difference is that an  $\Omega$ -type doubling parameter p on the order of B is possible if  $\epsilon \omega_2$  is on the order of A.

For the  ${}^{2}\Delta_{5/3,3/2}$  vibronic states, formulae for the rotational levels for any coupling case intermediate between (a) and (b) were shown by Hougen (35) to be of a form identical to the Hill-Van Vleck formula for spin uncoupling in a diatomic molecule. Hence, neglecting centrifugal distortion and  $\Lambda$  doubling, the rotational levels of the  ${}^{2}\Delta$  states for the case of  $A > \epsilon \omega_{2}$  and >BJ will be essentially the same as those of the  ${}^{2}\Pi$  electronic state without the Renner-Teller effect. Since the excitation of the bending vibration has little effect on the rotational structure of the  $X^{2}\Sigma$  electronic ground state, we conclude that the rotational structure of the (0, 1, 0)-(0, 1, 0) bands will be quite similar to that of the (0, 0, 0)-(0, 0, 0) bands but with a doubling of the number of levels associated with the two spin-orbit-split subgroups.

Thus, we are led to look for the (0, 1, 0)-(0, 1, 0) bands with doubled bandheads separated by roughly  $(\epsilon \omega_2)^2 / A$ . Figure 2 shows an "extra" bandhead at about 626.5 nm to the red of the (0, 0, 0)-(0, 0, 0) head of the  $A^2 \Pi_{1/2}$  subgroup of bands. No such bandhead appears on the red side of the  $A^2 \Pi_{3/2}(0, 0, 0)-(0, 0, 0)$  bandhead. A high-resolution scan of the spectral region on the red side of the  $A^2 \Pi_{1/2}(0, 0, 0)$ bandhead shows a *P*-type bandhead with about the intensity expected for a transition pumped from the (0, 1, 0) ground-state levels. This bandhead is located at 15 957.02(1) cm<sup>-1</sup>. We tentatively identify that bandhead as the  $P_1$  and  $Q_{12}$  head of the  $A\mu^2\Sigma - X^2\Pi$  (vibronic) transition.

Examination of the high-resolution spectra taken just to the blue of the (0, 0, 0)-(0, 0, 0) bandhead shows another weak bandhead near 15 966.75(1) cm<sup>-1</sup>, which we tentatively identify as the  $P_1$  and  $Q_{12}$  bandhead of the  $A^2\Delta_{3/2}-X^2\Pi$  (vibronic) transition. The wavenumber interval between these heads yields a Renner-Teller splitting of 9.73(2) cm<sup>-1</sup>.

In the  $A^2\Pi_{3/2}$  (electronic) group of lines, a weak bandhead tentatively ascribed to the  $A^2\Delta_{5/2}-X^2\Pi$  (vibronic)  $P_{21}$  and  $Q_2$  bandhead is found at 16 034.08(1) cm<sup>-1</sup>, which is approximately the location expected from the identification of the  $P_1$  bandheads and Hougen's analysis. However, no clearly identifiable bandhead is found near 16 044 cm<sup>-1</sup>, where the  $A\kappa^2\Sigma - X^2\Pi$  (vibronic) head should be found.

In CaOD, the corresponding features are found at 15 958.22(1) cm<sup>-1</sup> (the  $A\mu^2\Sigma$ - $X^2\Pi$  (vibronic) bandhead) and at 15 962.75(1) cm<sup>-1</sup> (the  $A^2\Delta_{3/2}-X^2\Pi$  (vibronic) bandhead). The separation between these heads yields a Renner-Teller splitting of 4.53(2) cm<sup>-1</sup>.

The ratio of the Renner-Teller splitting in CaOH to that in CaOD is 2.1 in agreement with the ratio of the squares of the bending vibration frequencies. Using the splittings given above and the bending vibration frequencies determined in Section III, we find the Renner parameters to be

 $\epsilon$ (CaOH) = 0.074(1),

$$\epsilon$$
(CaOD) = 0.072(1).

The smallness of the Renner parameter is easily understood: The bending vibration, because of the very small mass of the proton or deuteron compared to the masses of the calcium and oxygen nuclei, consists essentially of the motion of the hydrogen atom relative to the Ca–O bond direction. Since the electron responsible for the optical transition is found in orbitals centered on or near the Ca atom, the motion of the hydrogen atom has little effect on the energy levels associated with that electron.

The Renner parameter in the  $(0, 1, 0) A^2 \Pi$  (electronic) state of SrOH was recently determined (18) to be 0.036 by a perturbation calculation of the observed spin-splitting constants in the  $B^2\Sigma$  state. This value is consistent with the values found for CaOH and CaOD and the argument given in the preceding paragraph. We expect the Renner interaction to be larger in CaOH than in SrOH because when the bending mode is excited, an electron in an orbital centered on the Ca atom in CaOH will feel a larger Coriolis force (and hence a larger Renner interaction (36)) than will the equivalent electron in SrOH.

## VII. CONCLUSIONS

This work and the recent work on SrOH (18) indicate that the electronic spectra of polyatomic molecules can be analyzed with the same high precision traditionally associated with the spectroscopy of diatomics. For future work, a high-resolution rotational analysis of <sup>2</sup>II states with the bending mode excited should produce invaluable information to aid in unraveling the still incompletely understood details

of the Renner-Teller interaction. A joint analysis of the  $B^2\Sigma$  and  $A^2\Pi$  states of CaOH and SrOH would permit a complete description of many interesting electronic perturbations in linear polyatomic molecules.

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