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Observation and spectroscopy of high-lying states of the CaOH radical: Evidence for a bent, covalent state

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The CaOH radical has been produced in a supersonic molecular beam by the reaction of water vapor with laser desorbed calcium. Three new electronic states, the $D\ ^2\Sigma^+$, $E\ ^2\Sigma^+$, and F states have been observed by laser induced fluorescence and resonance enhanced multiphoton ionization spectroscopy. The D and E states are linear, but the F state is bent, the first bent and strongly covalent state of CaOH to be observed. Vibrational constants for the D state have been determined and a partially rotationally resolved spectrum has provided the rotational constant and Ca–OH bond length in this state. The D and E states are more strongly bound than the ground state, perhaps indicating some covalent contribution to the bonding. Additional vibrational constants of the ground electronic state including the CaO–H vibrational frequency have been determined from the emission spectra. © *1996 American Institute of Physics.* [S0021-9606(96)00746-5]

I. INTRODUCTION

The spectroscopy of the free radical alkaline earth monohydroxides, CaOH, SrOH, etc. is a subject that has been of interest since 1983 when Hilborn *et al.*[1] reported the observation and spectroscopy of CaOH produced in a Broida-type oven.[2] These species are interesting because they appear in flames,[3] are supposed to appear in circumstellar shells,[4] and can act as reaction intermediates. Hilborn[1] and co-workers carried out the first spectroscopic study of the $A\ ^2\Pi - X\ ^2\Sigma^+$ electronic transition of CaOH. They found the molecule to be linear in both ground and electronic excited states and gave a set of spectroscopic parameters for both the protonated and deuterated radicals. Wormsbecher *et al.*[5] observed the $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ transition in the chemiluminescence reaction of Ca with water, and Bernath and Kinsey-Nielsen[6] determined the rotational structure of the 000–000 and 100–100 transitions of this system. Jarman and Bernath[7] observed the electronically forbidden $C\ ^2\Delta - X\ ^2\Sigma^+$ transition which is made allowed through vibronic coupling.

Many experimental studies have been carried out to characterize these states.[8–17] Transitions between the ground state and the A, B, and C states all occur in the visible, the electronic transition energy being 15 998,[1] 18 022,[6] and 21 907 (Ref. 7) cm^{-1} for the $A-X$, $B-X$, and $C-X$ transitions, respectively. Prior to this work the X, A, B, and C states were the only electronic states of CaOH to have been observed.

There have been several theoretical calculations of the excited electronic states of CaOH.[18–21] The ground electronic state of CaOH is largely ionic consisting of a closed shell OH^- anion and a Ca^+ cation containing a 4*s* unpaired electron and a closed shell argon core. The low-lying excited electronic states of CaOH are also ionic involving excitation of the unpaired electron to excited orbitals of Ca^+, although Allouche and Aubert-Frécon[20] propose that the A and B states "may have a non-negligible contribution from covalent configurations." The X, A, B, and C states are all linear as would be expected of ionic states.

It should be noted that although CaOH is ionic, the dipole moments of the lower states are not particularly large (the dipole moments of the X, $A\ ^2\Pi_{1/2}$, $A\ ^2\Pi_{3/2}$, and B states are[8] 1.465, 0.836, 0.766, and 0.744 D, respectively) due to the large polarization of the unpaired electron away from the OH^-.

Supersonic jet spectroscopy has proven to be an excellent technique to obtain simplified spectra of polyatomic molecules.[22] The use of laser desorption coupled with supersonic expansions has allowed the study of molecules which were not accessible by other means due to their very low vapor pressures and/or their fragility at temperatures necessary to give a detectable signal.[23] The production of free radicals in a supersonic jet environment has been carried out in several ways.[24–27] Recently, Whitham *et al.*[27] produced CaOH and other radicals through the reaction of the laser desorbed metal vapor with water and other gases. The same technique was used by Steimle *et al.*[8] to carry out an optical Stark study of the radical and has been used in this work to study the high lying electronic states.

In this paper we report the observation of three near-ultraviolet transitions between the ground and higher lying electronic states of the CaOH radical. The highest of these three states is bent and is the first electronic state of CaOH that is largely nonionic.

II. EXPERIMENT

The free radical CaOH was produced by laser desorbing calcium metal into a helium carrier gas which contained water vapor. The high pressure mixture was expanded through a supersonic nozzle and both resonance enhanced multiphoton ionization (REMPI) and laser induced fluorescence (LIF) were used to investigate the system.

The experimental apparatus used in this work has been described in detail elsewhere[23] and only a brief description

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will be given here. In the REMPI experiments the supersonic jet produced by a pulsed solenoid valve was skimmed with a 1.0 mm skimmer placed about 4 cm from the nozzle. The molecular beam formed by the skimmer passed into a second chamber containing a reflectron time of flight mass spectrometer. The output of a Nd-YAG pumped dye laser was doubled or mixed with the 1.06 μ fundamental of the Nd-YAG laser and crossed with the molecular beam in the center of the acceleration region of the mass spectrometer. Several dyes (Fluorescein 548, DCM, LDS698) and a dye mixture (DCM/LDS698) were used to probe the spectral region of interest. Spectra were taken monitoring the parent mass of the radical.

Fluorescence experiments were done using an unskimmed free jet with the time-of-flight mass spectrometer replaced by fluorescence collection optics. Fluorescence excitation spectra were measured using f/1 optics which imaged the fluorescence onto a slit with an RCA 8575 photomultiplier tube immediately behind it. Dispersed fluorescence was also detected using f/1 optics which imaged the fluorescence onto the entrance slit of a Spex 1 m monochromator having an RCA 4501 photomultiplier tube at the exit slit. Both total and dispersed fluorescence could be collected at the same time. Excitation of the free jet occurred about 2 cm from the nozzle. For the rotationally resolved scans an excimer pumped dye laser (DMQ dye) with 0.2 cm^{-1} bandwidth was used for excitation.

A calcium metal rod of 1 in. diam and 1 in. length was prepared by melting Ca pieces inside an alumina holder using an argon atmosphere to avoid oxidation of the metal. A disk of about 2 mm thickness was cut and attached to a sample holder using cyanoacrylate ester. The calcium disk was then machined to make sure that the holder and the Ca surfaces were parallel. The disk could be rotated and translated at the same time to provide fresh areas of sample for vaporization, but translation was required only when a deep groove in the sample occurred. Failure to have the holder and metal surfaces parallel produced periodic signal fluctuation as the calcium disk was rotated. When these surfaces were parallel, the signal fluctuation was less than 15%.

Calcium from this disk was vaporized using the second harmonic of a Nd-YAG laser that was attenuated to 1 mJ per pulse using a 0.1 M $CoSO_4$ solution. The desorption laser was focused onto the calcium disk with a 50 cm focal length lens. The vapor of the metal was injected into a mixture of helium gas and water vapor. For most of the experiments the helium pressure was around 8 atm and the water vapor was at its room temperature vapor pressure.

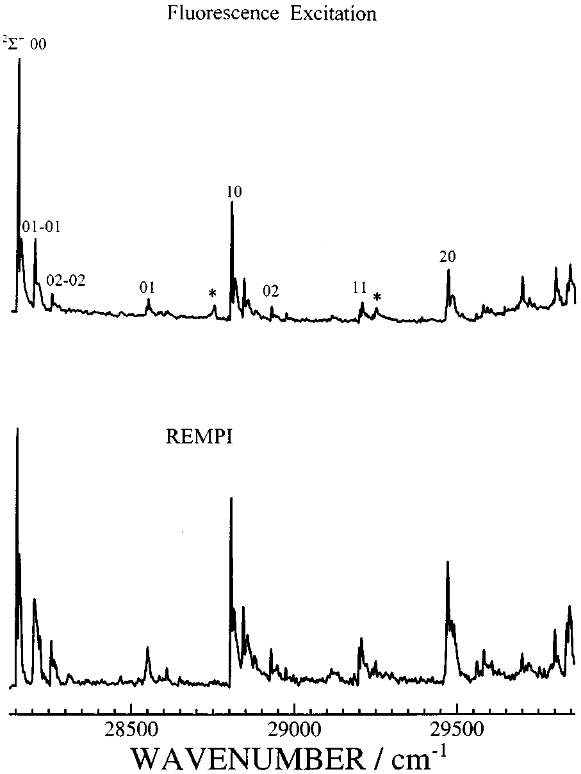

FIG. 1. Fluorescence excitation (top) and one color REMPI (bottom) spectra of the CaOH radical in the range 28 150–29 850 cm^{-1} showing the band system $D\ ^2\Sigma^+ - X\ ^2\Sigma^+$ of CaOH and the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ system of CaO (indicated by asterisks). In the case of CaOH the quantum numbers of the Ca–OH stretch and the bend are indicated. The third quantum number corresponding to the CaO–H stretch is omitted. When the vibrational quantum numbers are listed for only one electronic state, the initial state of the transition is the zero-point level of the ground electronic state.

III. RESULTS AND DISCUSSION

A. CaOH production

It should be noted that there is some uncertainty regarding the mechanism responsible for CaOH production. The most obvious reaction

$$Ca+H_2O=CaOH+H$$

is 0.96 eV endothermic.[28] It is possible (though unlikely) that calcium desorbs with this much kinetic energy, but it is almost certainly relaxed by collisions with helium before reacting to form CaOH. Moreover, calcium produced in a Broida oven is known to react with water vapor to produce CaOH,[1] and in these circumstances the calcium could not have sufficient energy to react directly. The puzzle regarding the reaction of alkaline-earth metals with water to produce metal hydroxides and even electronically excited metal hydroxides has been previously noted.[5]

In addition to CaOH, we also observe spectral features from CaO produced in the reaction of calcium with water. The CaOH and CaO spectra are not optimized under the same conditions. CaO is favored by relatively high (e.g., 28 atm) helium pressure and CaOH is favored by relatively low (e.g., 8 atm) helium pressure. There is also a question regarding the mechanism of production of CaO since the reaction

$$Ca+H_2O=CaO+H_2$$

is 0.92 eV endothermic.[29]

B. The *D* state of CaOH

Figure 1 shows the REMPI and fluorescence excitation spectra of the CaOH radical in the range 28 150–29 850 cm^{-1}, and the wave numbers of the transitions of these spec-

TABLE I. Wave numbers (cm^{-1}) for the assigned bands of CaOH (except as noted) that appear in the excitation spectra of Figs. 1 and 2. Vibrational modes are listed in the order, Ca–OH stretch, bend, CaO–H stretch.

Wave number	$D\ ^2\Sigma^+ - X\ ^2\Sigma^+$	$E\ ^2\Sigma^+ - X\ ^2\Sigma^+$	$F\ ^2\Pi - X\ ^2\Sigma^+$	$C\ ^1\Sigma^+ - X\ ^1\Sigma^+$
28 153	000–000			
28 207	010–010			
28 261	020–020			
28 565	010–000			
28 776				0–0, CaO[a]
28 828	100–000			
28 949	020–000			
29 225	110–000			
29 269				1–0, CaO[a]
29 486	200–000			
29 874				2–0, CaO[a]
29 879		000–000		
30 134	300–000			
30 215			000–000	
30 617		100–000		

[a] Reference 30.

tra are given in Table I. The total fluorescence spectrum is shown at the top of the figure while the REMPI spectrum is shown at the bottom to facilitate comparison. The mass selected spectrum reproduces most of the features appearing in total fluorescence. The peaks marked with asterisks appearing at 28 776, 29 269, and 29 874 cm^{-1} in total fluorescence are assigned to the 0–0, 1–0, and 2–0 bands, respectively, of the $C\ ^1\Sigma^+ - X\ ^1\Sigma^+$ electronic transition of the CaO molecule.[30] Changing the helium backing pressure allowed us to optimize the production of CaOH against CaO.

The band appearing at 28 153 cm^{-1} is assigned as the origin of a transition to a previously unobserved electronic state. The emission spectrum produced by excitation of this band is shown in the top spectrum of Fig. 2, and the wave numbers of the features in this spectrum are given in Table II. We observed no features to the red of this band which could not be assigned to transitions involving previously identified states. This band is shown at higher resolution in Fig. 3. The rotational structure shows a P branch head and a violet degraded R branch with no Q branch. This is consistent with a transition from the $X\ ^2\Sigma^+$ state to a new $^2\Sigma^+$ state. The spin-rotation splitting characteristic of a $^2\Sigma - ^2\Sigma$ transition is just observable in some of the R branch features. Ortiz[18] calculated a $D\ ^2\Sigma^+$ state with transition energy of 26 495 cm^{-1}. The 28 153 cm^{-1} band being the closest new feature to the calculation of Ortiz, we assign this band as the origin of the $D\ ^2\Sigma^+ - X\ ^2\Sigma^+$ transition. In addition to the origin transition, we observe progressions involving both the Ca–OH stretching vibration and the bending vibration and sequences in the bending vibration. These are marked on Fig. 1. For nontotally symmetric vibrations such as the bend, the selection rule for an allowed transition is $\Delta v = \text{even}$. In addition to such allowed transitions, we also see two weak $\Delta v_2 = 1$ transitions presumably made allowed by vibronic coupling in the excited state. Such vibronically allowed transitions have been previously observed in other electronic transitions of CaOH.

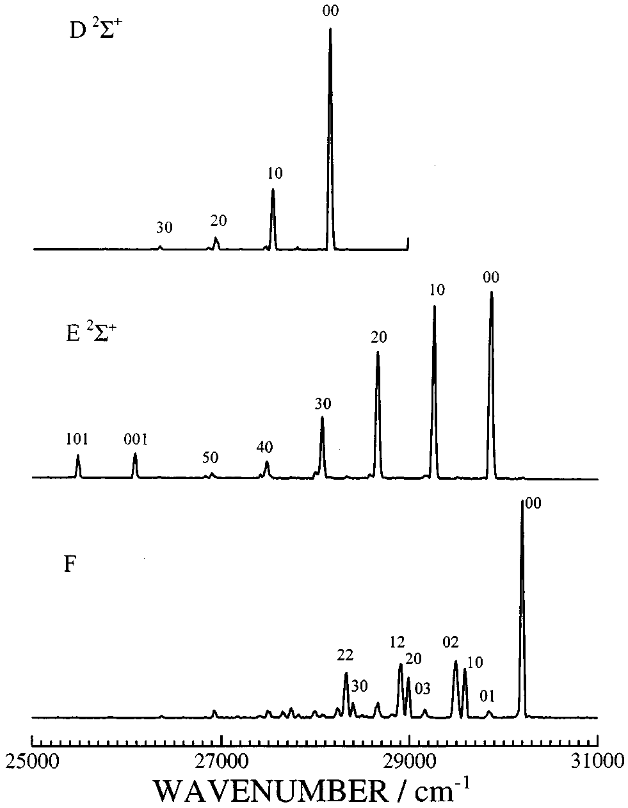

FIG. 2. Emission spectra of the three band origins of the three electronic states observed in this work. (Top) Emission from $D\ ^2\Sigma^+$; (middle) emission from $E\ ^2\Sigma^+$; and (bottom) emission from F. The quantum numbers for the ground electronic state of the Ca–OH stretch, the bend, and the CaO–H stretch are indicated. Where only two quantum numbers appear, the third quantum number of the CaO–H stretch is zero and has been omitted.

Figure 4 shows the vibrational levels of the $D\ ^2\Sigma^+$ state that have been directly observed in this work. Table III gives the molecular parameters obtained for this electronic state which were determined from the energy level structure given in Fig. 4 and a fit to the formula[31]

$$E = T_0 + w_1 v_1 + w_2 v_2 + x_{11} v_1^2 + x_{22} v_2^2 + x_{12} v_1 v_2 .$$

We neglect the terms corresponding to the CaO–H stretching mode, as well as terms involving the angular momentum of the degenerate bending vibration. The w_1 and x_{11} molecular constants listed in Table III have been determined with one degree of freedom in the estimated error, while w_2, x_{22}, and x_{12} have been estimated with no degrees of freedom in the estimated error.

The rotational structure shown in Fig. 3 has been analyzed. Assuming[12] a value for the ground state of $B''(X\ ^2\Sigma) = 0.334\ 33\ \mathrm{cm}^{-1}$, the rotational constant of the excited state is $B'(D\ ^2\Sigma) = 0.364\ 45\ \mathrm{cm}^{-1}$. Using the relationship between the bond lengths and the rotational constant[16] and assuming that the value of the bond length $R(\text{CaO–H})$ is the same in the D state as it is in the A state[16] (0.9572 Å), the

TABLE II. Wave numbers (cm^{-1}) of the bands appearing in the emission spectra for different excitatiion features of CaOH. Wave numbers are given as red-shifts relative to the excitation wave number.

Vibrational assignment[a]	28 153[b]	29 879	30 215	30 311	30 366	30 617	Average
010			356	363	350	347	354
100	604	603	608	611			606
020	679	671	700	690	688		686
110				954	951		952
200	1204	1207	1213	1211	1207	1201	1207
120		1280	1289	1295	1296	1270	1286
040					1389		1389
210			1533	1541	1543		1539
130					1626		1626
300	1797	1794	1806	1803	1794	1806	1800
220		1865	1875	1876	1871	1872	1872
140			1967	1964	1968		1966
310				2124	2128		2126
230				2203			2203
400		2376		2383		2384	2381
320		2452		2457	2459	2459	2457
410					2702		2702
500		2961				2961	2961
001		3779				3777	3778
101		4384					4384
201		4974				4963	4969
121						5029	5029
301		5567				5545	5556
221						5604	5604
401						6133	6133
321						6196	6196

[a] Vibrational quantum numbers of the X electron state in the order Ca–OH stretch, bend, CaOH–H stretch.
[b] Wave number of the excitation transition.

Ca–OH bond length in the D state is 1.894 Å, approximately 5% less than the Ca–OH bond length in the ground state (1.982 Å).

Finally, we should comment on the rotational and vibrational temperatures inferred from the $D-X$ fluorescence excitation spectrum. Since the ground electronic state has a bending frequency of 352 cm^{-1}, we were surprised to see relatively intense sequence transitions in the bending mode in the cold environment of a supersonic free jet. The intensities of the sequence transitions are fairly well described by a vibrational temperature of 277 K. As is usually the case, the intensities of the rotational structure in the 0–0 band are not well described by a single rotational temperature, the

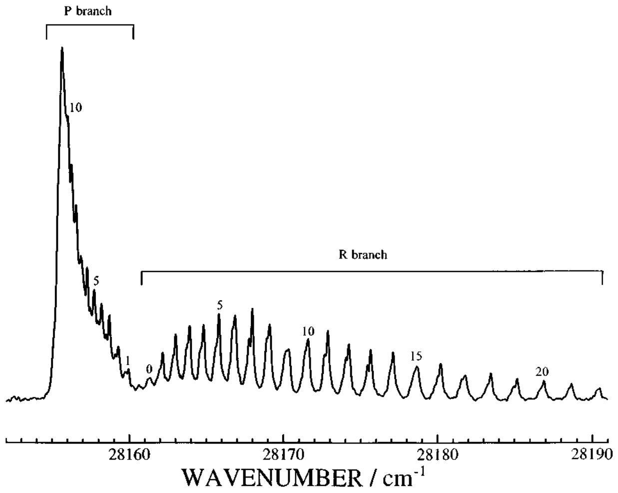

FIG. 3. Fluorescence excitation rotationally resolved spectrum of the band origin of the $D\ ^2\Sigma^+-X\ ^2\Sigma^+$ system of CaOH. The value of J for several of the $P(J)$ and $R(J)$ branch features is indicated. The intensity pattern of the rotational levels yields a rotational temperature of 40–50 K.

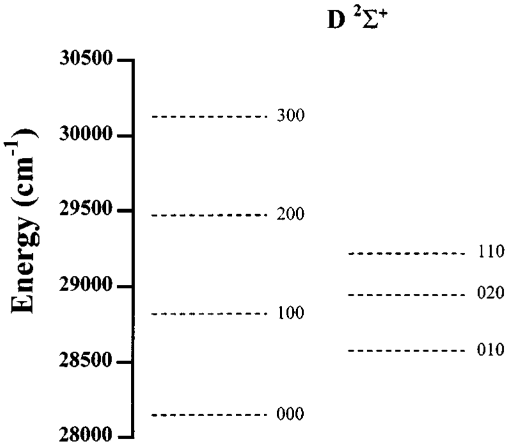

FIG. 4. Schematic diagram of the vibrational levels of the $D\ ^2\Sigma^+$ state that have been directly observed in this work and that give the molecular constants listed in Table III.

TABLE III. Molecular parameters for the excited state $D\ ^2\Sigma^+$ of CaOH determined from the observed energy levels shown in Fig. 3.

Parameters	Value/cm^{-1}	Std. Err/cm^{-1}
w_1	681.0	1.5
w_2	425.6	2.1
x_{11}	−6.9	
x_{22}	−13.6	
x_{12}	−13.9	

high-J, R-branch transitions having too much intensity for a Boltzmann distribution at a temperature that fits the low-J transitions. If the rotational distribution is to be characterized by a single rotational temperature fit to the low-J transitions, that temperature is between 40 and 50 K. Again, this is a higher rotational temperature than is usually seen in a supersonic expansion.

However, such high temperatures are not unknown. Cai *et al.*[32] reported a rotational temperature of 14 K and a vibrational temperature of 4000 K for jet cooled AlO prepared by the reaction of laser vaporized aluminum with various oxidants. Vibrational relaxation is an inefficient process requiring many collisions with the carrier gas. If the hot seed gas is present in the original gas mixture, it undergoes a relatively large number of collisions between the throat of the nozzle and the point of observation. However if the hot seed gas is formed by means of a chemical reaction somewhere downstream of the throat, the number of collisions with the carrier gas is reduced producing less complete vibrational cooling. Rotational relaxation requires fewer collisions, but again, if the rotationally hot seed is formed downstream in the expansion, there will be less rotational cooling.

It is possible that this is also the reason for our observation of vibrationally and rotationally hot CaOH. However, we note that we also observed vibrationally hot CaO (up to $v''=6$ in the 732 cm^{-1} vibration) when the CaO was laser desorbed from solid CaO prior to any expansion. In this case there was no chemical reaction, and the hot vibrational distribution must have been produced in the laser desorption process and not completely relaxed even by the large number of collisions between the desorption in the nozzle and the point of observation.

C. The *E* state of CaOH

Figure 5 continues the REMPI and fluorescence excitation spectra of CaOH to higher wave numbers than shown in Fig. 1. There is an intense feature at 29 879 cm^{-1} that we assign as the origin of a transition to a new $^2\Sigma^+$ electronic state. Although we have not observed this feature at high enough resolution to resolve rotational structure, the band profile shows a P-branch head and a violet degraded R branch with no Q branch. The emission spectrum observed upon excitation of this feature is shown in the middle spectrum of Fig. 2 and consists of a long progression in the Ca–OH stretch with only very weak features involving even harmonics of the bend. This emission spectrum also shows the first member of a progression involving the CaO–H stretch, the first time this mode has been observed in a CaOH emission spectrum. Both the rotational profile and the emission spectrum resemble those of the $D-X$ origin transition, but the intensity and frequency of this feature fit neither the intensity profile nor the expected frequency of a progression built on the $D-X$ origin. Ortiz[18] calculated the E state as a $^2\Sigma^+$ state at 29 860 cm^{-1} which further supports our assignment of the 29 879 cm^{-1} feature as the origin of the $E-X$ transition.

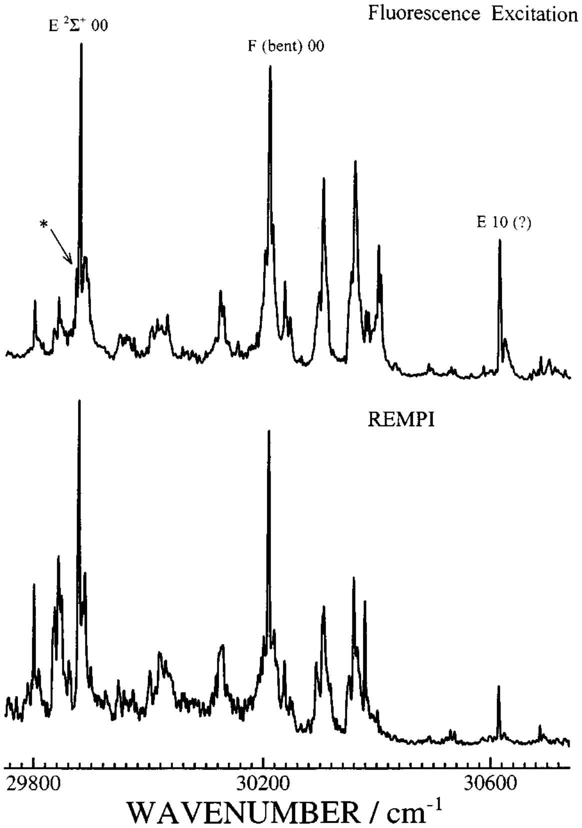

FIG. 5. Fluorescence excitation (top) and one color REMPI (bottom) spectra of CaOH in the range 29 760–30 720 cm^{-1}. A feature due to CaO is indicated by an asterisk. The quantum numbers of the Ca–OH stretch and the bend are indicated. The third quantum number corresponding to the CaO–H stretch is omitted. The initial state of the marked transitions is the zero-point level of the ground electronic state.

We have not been able to unambiguously assign vibrational progressions built on the $E-X$ origin because the spectrum becomes crowded at higher frequencies, and the possibility of vibronic mixing of the E and F (see below) states makes interpretation of the spectrum more difficult. There is a feature at 30 617 cm^{-1} whose rotational profile resembles that of a $^2\Sigma^+$–$^2\Sigma^+$ transition and which might be the first member in the Ca–OH stretching progression. The emission spectrum obtained by exciting this feature is shown in Fig. 6. The emission spectrum shows a lot of activity in the Ca–OH stretch but also shows activity in the bend including transitions to odd v'' states perhaps caused by mixing with the F state. Moreover, this emission spectrum also shows the first member of a progression in the CaO–H stretch and combination bands built on this third fundamen-

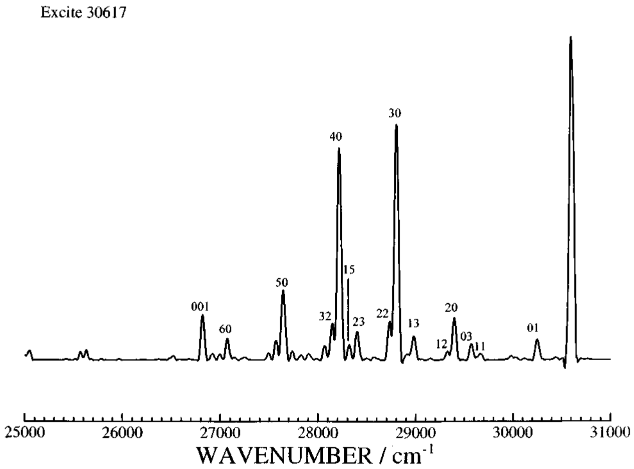

FIG. 6. Emission spectrum of the feature at 30 617 cm^{-1} tentatively assigned to the first member of the Ca–OH stretching progression of the $E\ ^2\Sigma^+ - X\ ^2\Sigma^+$ system. The quantum numbers for the ground electronic state of the Ca–OH stretch, the bend, and the CaO–H stretch are indicated. Where only two quantum numbers appear, the third quantum number of the CaO–H stretch is zero and has been omitted.

tal. The fluorescence excitation spectrum of CaOD has corresponding features at 29 905 and 30 628 cm^{-1} which might be assigned to the $E-X$ origin and first Ca–OD stretching progression. Emission from both of these states also shows activity in all three vibrations. If these assignments are correct, the $v'=0-v'=1$ spacing is 738 cm^{-1} in CaOH and 723 cm^{-1} in CaOD indicating that the Ca–OH stretching frequency is higher in the E state than in any of the previously observed states. This might be an indication of increased covalent bonding in the E state.

D. The *F* state of CaOH

The feature at 30 215 cm^{-1} is quite different from any of the bands at lower frequencies. First, the rotational profile of this band shows a strong central Q branch in addition to the P and R branches. Second, the emission spectrum produced by excitation of this feature (bottom spectrum of Fig. 2) shows not only extensive activity in the Ca–OH stretching vibration but also extensive activity in the bending vibration. Transitions to even v'' states are more intense, but transitions to odd v'' states are clearly visible. Ortiz calculated a $^2\Pi$ state at 30 010 cm^{-1}. The rotational P, Q, R rotational profile would be consistent with a $^2\Pi - ^2\Sigma^+$ transition, although one would expect a second strong transition to a second fine-structure state. However, the extensive activity in the bending vibration is not consistent with a transition between two linear states. It seems likely that the feature at 30 215 cm^{-1} is the $F-X$ origin, but that the F state is bent. CaOH has always been regarded as an ionic molecule and therefore only linear states have been considered. At some point of excitation one would expect bent, covalent states involving p orbitals on the oxygen, and the feature at 30 215 cm^{-1} appears to be a transition to the first of these states.

The region above the $F-X$ origin is congested and (with the possible exception discussed above) remains unassigned.

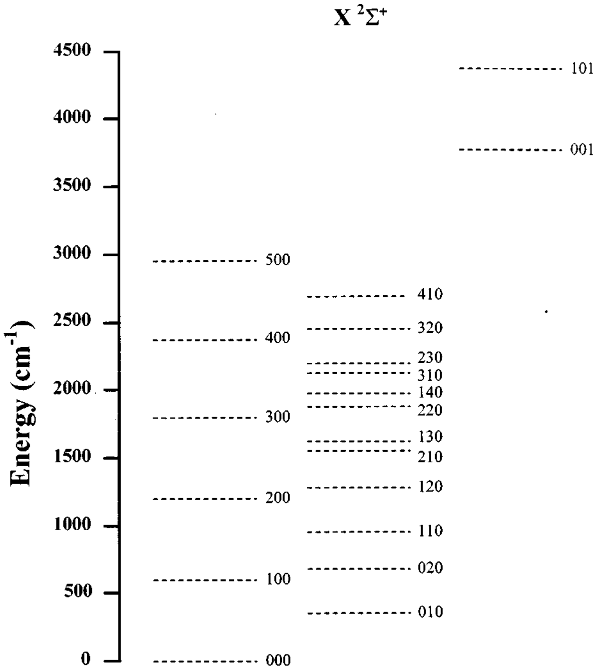

FIG. 7. Schematic diagram of the vibrational levels of the $X\ ^2\Sigma^+$ state that have been observed in this work and that give the molecular constants listed in Table IV.

Since the E and F states are only separated by 336 cm^{-1}, extensive mixing between these two states would be expected as well as possible mixing with other ionic and covalent states that might be in this region. Therefore, further assignment of the spectrum may be difficult without considerably more work.

E. Ground state vibrational constants

Coxon[9,14] and co-workers have determined the frequencies for a number of emission features and have used this information to extract vibrational constants for the ground electronic state of CaOH. The precision of the previous work was greater than ours. However, using emission from the origins of the $D-X$, $E-X$, and $F-X$ transitions, and from the features at 30 311 and 30 366 cm^{-1}, we were able to observe transitions to more and higher vibrational levels of the ground state as shown in Fig. 7. The extensive activity in the bending mode observed in emission from the features at 30 215 (F origin), 30 311, and 30 366 cm^{-1} (see Table II) were particularly important in allowing us to measure previously unobserved vibrational levels in the ground electronic state. We were therefore able to obtain estimates of additional anharmonic constants. The vibrational spectroscopic constants extracted from our data and the values from Refs. 9 and 14 are given in Table IV.

Of particular importance is the first measurement of the CaO–H fundamental frequency obtained from the emission spectra of the E state. This frequency is 3778 cm^{-1} in CaOH and 2790 cm^{-1} in CaOD. This is very close to the vibrational frequency[33] of OH^- which is 3738 cm^{-1}. We note that the

TABLE IV. Molecular parameters for the ground state of CaOH determined from the observed energy levels shown in Fig. 7.

Parameters	Value/cm^{-1}	Std. Err./cm^{-1}
ν (CaO–H)	3778	
ν (CaO–D)	2790	
w_1	610.4(612.8)[a]	2.0
w_2	350.0(352.9)[b]	2.5
x_{11}	−3.7(−3.74)[a]	0.8
x_{22}	−0.8	0.6
x_{12}	−7.1	0.7

[a] Reference 9.
[b] Reference 14.

assumption of Li and Coxon[16] that the CaO–H stretching frequency is the same as the OH$^-$ frequency is correct.

IV. CONCLUSIONS

The electronic spectrum of the CaOH radical in the UV region has been investigated through REMPI and LIF spectroscopy and three new electronic states have been observed. The vibrational structure of the $D\ ^2\Sigma^+$ excited state has been analyzed and a set of molecular constants for this state has been determined. The partially rotationally resolved spectrum of the band origin of this state has provided the rotational constant and Ca–OH bond length. The $D\ ^2\Sigma^+$ and $E\ ^2\Sigma^+$ states are linear and more strongly bound than the ground state. These states are probably largely ionic but may have a non-negligible covalent component. The F state is bent and the first strongly covalent state observed for CaOH. The dispersed emission spectra have allowed the determination of additional vibrational molecular constants of the ground electronic state including the vibrational frequency of the CaO–H stretch.

ACKNOWLEDGMENTS

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