SPECTROSCOPY OF CaOH

P. F. BERNATH AND C. R. BRAZIER
Department of Chemistry, University of Arizona
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ABSTRACT

High-resolution laser spectroscopy of CaOH has produced accurate spectroscopic constants for the $B\ ^2\Sigma^+$, $A\ ^2\Pi$, and $X\ ^2\Sigma^+$ states of CaOH. The pure rotational transition frequencies of the ground state are predicted.

Subject headings: laboratory spectra — molecular processes

I. INTRODUCTION

Metal hydroxide molecules are of considerable astrophysical interest. The calculations of Tsuji (1973) predict that monohydroxides and monochlorides form the major alkali, alkaline earth, and aluminum species in cool stars. CaCl bands are prominent in carbon and SC type stars, and there has been a tentative detection of the $B\ ^2\Sigma^+$–$X\ ^2\Sigma^+$ absorption band of CaOH in late-type M dwarf stars (Pesch 1972). Clegg and Wootten (1980) have searched for AlCl in circumstellar envelopes.

The possibility of metal hydroxide molecules occurring in the interstellar medium has also been considered, and two different production schemes have been proposed. Smith *et al.* (1983) suggest that NaOH could be formed from the recombination of the cluster ion $Na^+ \cdot H_2O$ with an electron. Duley and Millar (1978) propose that metal ions (such as Na^+ and Ca^+) can react with O^- and OH^- surface defect centers of interstellar grains. The M^+OH^- binding energy can be released to the bulk of the grain, or some of the energy can be used to eject MOH into the gas phase. Duley and Millar predict that Ca^+ ions, in contrast to Na^+, have a very high probability of sticking to oxide grain surfaces. Hence, grains should deplete Ca^+ ions more than Na^+ and by implication produce considerably more gas phase NaOH than CaOH. Because metal atomic ions generally react and recombine more slowly than molecular ions, their abundances can be relatively high inside molecular clouds; consequently they may play a significant role in the overall ionization balance. The observation of metal containing hydroxides may provide insight into the chemistry of molecular clouds and the underabundance of gas phase metals relative to hydrogen.

The optical emission spectrum of CaOH has been known for many years. Reddish and greenish emission from CaOH occurs when calcium salts are added to flames (James and Sugden 1955; Weeks, Haraguchi, and Winfordner 1978). By analogy with the isoelectronic molecule CaF the green emission near 5550 Å can be assigned to the $B\ ^2\Sigma^+$–$X\ ^2\Sigma^+$ transition while the 6220–6270 Å bands belong to $A\ ^2\Pi$–$X\ ^2\Sigma^+$. Harris and co-workers (Wormsbecker *et al.* 1983) were able to make CaOH in a Broida type oven (West *et al.* 1975) and to rotationally analyze the 000–000 (Hilborn, Zhu, and Harris 1983) band of the $A\ ^2\Pi$–$X\ ^2\Sigma^+$ system. CaOH and CaOD proved to be linear molecules. Bernath and Kinsey-Nielsen (1984) then rotationally analyzed the 000–000 and 100–100 bands of the $B\ ^2\Sigma^+$–$X\ ^2\Sigma^+$ system.

In order to characterize more thoroughly the $A\ ^2\Pi$–$X\ ^2\Sigma^+$

transition, we have recently observed some additional lines. The results of a weighted nonlinear least-squares fit of all the available CaOH data are reported here. We believe that our $X\ ^2\Sigma^+$ constants predict the lower-frequency microwave transitions to an accuracy of about 10 MHz.

II. METHOD

The production of CaOH in a Broida oven has been described by Bernath and Kinsey-Nielsen (1984). In brief, CaOH was produced by reacting Ca with H_2O at a total pressure of about 7 torr of mainly argon carrier gas.

The output of a computer-controlled ring dye laser (Coherent 699–29) was focused into the weakly chemiluminescent CaOH flame. The dye laser was operated with DCM dye pumped by 7 W of the 4880 Å line from a Coherent Innova 20 argon ion laser. The laser induced CaOH fluorescence was focused onto the slits of a 0.65 meter monochromator and detected with a cooled photomultiplier tube with photon counting electronics.

The spectra were detected by scanning the laser and recording the fluorescence through the monochromator. This acted as a filter to simplify the excitation spectrum by recording only the lines of interest (Linton 1978; Dulick, Bernath and Field 1980; Hilborn, Zhu, and Harris 1983). This technique was necessary because the spectrum (see Fig. 1) was badly overlapped.

Three channels of data were recorded on floppy disk: the laser excitation spectrum, an I_2 calibration spectrum, and fringes of a 6 GHz Fabry-Perot interferometer from the Coherent 699–29 wavemeter. The Fabry-Perot fringes served only as a monitor to verify that the scans were continuous. The I_2 spectrum (Gerstenkorn and Luc 1978) was used to calibrate periodically the wavelength scale provided by the wavemeter. The data were not corrected by subtracting $0.0056\ cm^{-1}$ from the observed lines (Gerstenkorn and Luc 1979).

III. RESULTS AND DISCUSSION

Although Herschel (1823) observed CaOH flame bands as early as 1823, the first rotational analysis was published by Hilborn, Zhu, and Harris in 1983. Figure 1 illustrates the problem. In the top panel is the laser excitation spectrum of the $B\ ^2\Sigma^+$–$X\ ^2\Sigma^+$ transition at 1 cm^{-1} resolution. The rotational temperature is about 500 K yet there is very little sign of band heads because of the dense sequence structure. The $A\ ^2\Pi$–$X\ ^2\Sigma^+$ bands are much clearer than the B–X bands at 500 K due to the presence of low $N\ Q$ heads (Hilborn, Zhu, and Harris
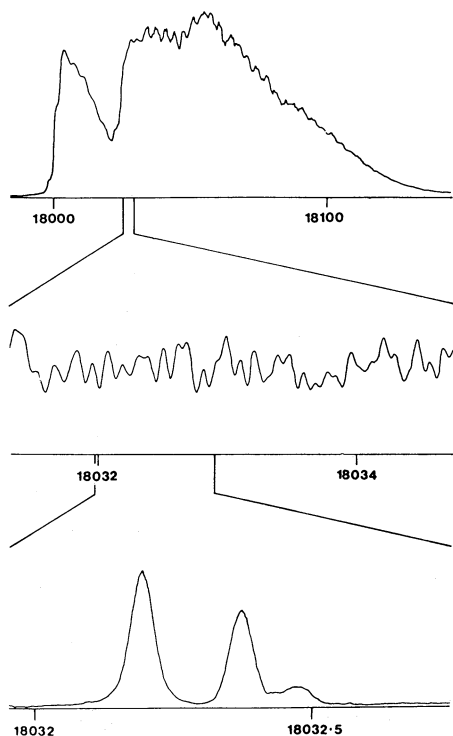
FIG. 1.—The top panel is a laser excitation spectrum of the $B\ ^2\Sigma^+$–$X\ ^2\Sigma^+$ transition of CaOH. This spectrum is equivalent to a 500 K absorption spectrum with about 1 cm^{-1} resolution. The center panel is a Doppler-limited Fourier transform emission spectrum, for which the baseline is at the bottom of the panel. Resolution is limited by the badly overlapped lines. The bottom panel is a laser excitation spectrum which has been simplified by selective excitation and selective fluorescence detection. Rotational analysis of the simplified spectrum was straightforward.

1983) whereas the B–X heads only occur at high N. However, at the temperatures found in flames or stellar atmospheres, the CaOH molecule has an almost featureless optical spectrum. The problem is not caused by lack of resolution. Panel 2 shows a CaOH emission spectrum taken at Doppler-limited resolution with the McMath Fourier transform spectrometer at Kitt Peak National Observatory. The lines are so dense that the spectrum is almost continuous (the baseline is at the bottom of the panel). Panel 3 shows how selective excitation with a dye laser and selective fluorescence detection is able to simplify the spectrum (Bernath and Kinsey-Nielsen 1984). The careful use of a monochromator as a fluorescence filter allows only the line of interest (for instance, the 000–000 band) to be detected and makes assignment easy. Classical spectroscopic techniques fail completely for CaOH.

The new 000–000 band $A\ ^2\Pi$–$X\ ^2\Sigma^+$ lines are presented in Table 1. The analysis of Hilborn, Zhu, and Harris was found to be essentially correct except for the high $J\ Q_2$ lines where the numbering had to be decreased by one. The R_2 branch was followed up to $J'' = 48.5$ where the satellite Q_{21} branch was almost completely resolved. The lines in these two branches are separated by $\gamma''(N + \frac{1}{2})$, where γ'' is the ground state spin rotation constant. (See Herzberg [1950] for energy level diagrams and notation for $^2\Pi$–$^2\Sigma^+$ transitions.) The lines $R_2(J)$ and $Q_{21}(J + 1)$ for $J = 43.5, 44.5, 46.5,$ and 48.5 were used to obtain $\gamma'' = 0.00111$ cm^{-1} with an estimated uncertainty of 0.0001 cm^{-1}. Only the R_2 lines were included in the final fit, de-

weighted by a factor of 16 relative to unblended lines, and γ was held fixed.

The $B\ ^2\Sigma^+$–$X\ ^2\Sigma^+$ 000–000 lines (Bernath and Kinsey-Neilsen 1984), Hilborn, Zhu, and Harris's (1983) $A\ ^2\Pi$–$X\ ^2\Sigma^+$ 000–000 lines and the lines in Table 1 were combined in a simultaneous nonlinear least-squares fit. Hilborn et al.'s data and all blended lines were deweighted by a factor of 16 (the square of the ratio of the estimated absolute accuracies). The $^2\Pi$ and $^2\Sigma^+$ states were represented by Zare et al.'s (1973) case (a) matrix elements. An explicit listing of these matrix elements can be found, for instance, in Kotlar et al.'s (1980) paper on CN. The resulting molecular constants are in Table 2.

The molecular constants for the $^2\Sigma^+$ states of Table 2 can be used with the traditional energy level expressions for $^2\Sigma$ states (Herzberg 1950) to predict the pure rotational transitions. The strong transitions with $\Delta N = \Delta J$ for $N'' < 9$ are listed in Table 3. Note that each line is split into two components separated by 33 MHz, the spin-rotation constant. The low N transitions also have reasonably strong Q branch satellite transitions. The first two occur at 20014 MHz and 40028 MHz. The satellite Q transitions decrease very rapidly in line strength as N increases (Herzberg 1950, p. 250).

The absolute accuracy of the predictions is not easy to estimate. The statistical uncertainty displayed by the molecular constants of Table 2 gives uncertainties of about 0.5 MHz for the $N = 1$–0 transition and about 5 MHz for the $N = 10$–9 transition. Based on previous experience with fits of this type, absolute uncertainties of 10 MHz ($J = 1$–0) to 100 MHz ($J = 10$–9) are much more realistic. The large number of systematically blended lines due to unresolved satellite transitions probably causes the statistical uncertainties to be an unreliable estimate of the overall uncertainties. Notice that there are small but definitely systematic residuals present in the fit to the lines of Table 1.

An additional complication is the possibility of proton hyperfine structure. CaOH is an ionic molecule so that the unpaired electron is in a $4s\sigma$ Ca$^+$-centered orbital. The unpaired electron density at the proton is thus rather small. An ESR spectrum of MgOH provides the Frosch and Foley parameters $b = 10.1$ MHz and $c = 4.8$ MHz (Brom and Weltner 1973). The CaOH molecule is more ionic than MgOH so that these numbers are probably upper limits. The effect of hyperfine parameters of this magnitude is to split the $N = 1$–0 transitions (both R and Q) into triplets spaced by about 5 MHz (for explicit $^2\Sigma$ hfs expressions see, for instance, Carrington, Milverton, and Sarre 1978). At high N the hyperfine structure will not be observed in the strong $\Delta N = \Delta J = \Delta F$ transitions because the hyperfine terms in the Hamiltonian produce constant N independent splitting of the energy levels.

There are no experimental or theoretical estimates of the dipole moment of CaOH but it should be large. The experimental dipole moments of CaF and CaCl are 3.07D (Childs et al. 1984) and 4.27D (Ernst, Kindt, and Törring 1983), respectively. From a comparison of alkali hydroxides with alkali halides, for which slightly more information is available, CaOH should have a dipole moment of 2 to 3D.

The predicted line frequencies presented here are probably accurate enough for a preliminary microwave search for CaOH in the interstellar medium and in oxygen-rich circumstellar envelopes. Although the absolute frequencies are somewhat uncertain, the spin-splitting is rather better determined, (± 3 MHz) so that detection of both spin doublet components with comparable strengths in the $N = 2$–1 and higher tran-

TABLE 1

ADDITIONAL LINE POSITIONS FOR THE 000–000 $A\ ^2\Pi$–$X\ ^2\Sigma^+$ TRANSITION OF CaOH

J	P_2	R_{21}	R_1	R_2
1.5	...	...	...	16031.931(8)
2.5	...	16034.328(8)	...	16032.327(10)
3.5	...	16035.406(5)	...	16032.734(5)
4.5	16026.295[a](−4)[b]	16036.502(6)	15970.372(−2)	16033.163(5)
5.5	16025.364(−9)	16037.612(2)	15971.464(−2)	16033.607(3)
6.5	16024.464(−2)	16038.742(0)	15972.561(−7)	16034.071(4)
7.5	16023.571(−4)	16039.894(4)	15973.678(−2)	16034.547(1)
8.5	16022.696(−4)	16041.058(3)	15974.802(−1)	16035.045(2)
9.5	16021.842(−2)	16042.243(6)	15975.936(−0)	16035.557(0)
10.5	16021.002(−2)	16043.439(2)	15977.077(−1)	16036.087(0)
11.5	16020.180(−1)	16044.655(2)	15978.228(−4)	16036.633(−0)
12.5	16019.375(−1)	16045.890(3)	15979.393(−2)	16037.197(−1)
13.5	16018.586(−1)	16047.140(3)	15980.569(0)	16037.775(−4)
14.5	16017.815(−1)	16048.406(1)	15981.749(−3)	16038.371(−5)
15.5	16017.061(−0)	16049.691(1)	15982.944(−1)	16038.983(−8)
16.5	16016.323(−0)	16050.992(1)	15984.148(−1)	16039.615(−7)
17.5	16015.602(−1)	16052.308(−0)	15985.365(0)	16040.263(−6)
18.5	16014.900(−0)	16053.644(−0)	15986.588(−0)	16040.928(−6)
19.5	16014.212(−1)	16054.998(2)	15987.819(−3)	16041.608(−6)
20.5	16013.543(−1)	16056.369(4)	...	16042.301(−10)
21.5	16012.891(−1)	16057.753(2)	15990.321(−0)	16043.012(−13)
22.5	16012.255(−1)	16059.156(3)	15991.587(1)	16043.749(−6)
23.5	16011.635(−2)	16060.576(3)	15992.859(−1)	16044.493(−8)
24.5	16011.035(−0)	16062.006(−2)	15994.144(−1)	16045.256(−9)
25.5	16010.452(1)	16063.465(2)	15995.440(0)	16046.033(−11)
26.5	16009.883(1)	...	15996.745(−0)	16046.829(−10)
27.5	16009.328(−2)	...	15998.059(−1)	16047.643(−7)
28.5	16008.794(−1)	...	15999.382(−3)	...
29.5	16008.278(0)	...	...	...
30.5	16007.780(3)	...	16002.066(−0)	...
31.5	16007.293(1)	...	16003.423(1)	...
32.5	16006.823(−0)	...	16004.789(1)	...
33.5	16006.372(−0)	...	16006.164(0)	...
34.5	16005.934(−2)	...	16007.549(−0)	...
35.5	16005.518(−0)	...	16008.944(−1)	...
36.5	16005.118(0)	...	16010.352(1)	16055.678(1)
37.5	16004.729(−3)	...	16011.768(0)	16056.653(5)
38.5	16004.365(1)	...	16013.193(−0)	16057.639(4)
39.5	16004.010(−1)	...	16014.630(−0)	16058.632(−4)
40.5	16003.675(−0)	...	16016.078(1)	16059.655(0)
41.5	16003.354(−2)	...	16017.534(−0)	16060.691(2)
42.5	16003.053(−0)	...	16019.002(0)	16061.737(−0)
43.5	16002.767(0)	...	16020.484(5)	16062.804(1)
44.5	16002.497(0)	...	16021.966(0)	...
45.5	16002.243(0)	...	16023.464(0)	16064.979(1)
46.5	16002.005(0)	...	16024.972(0)	16066.088(0)
47.5	16001.786(2)	...	16026.492(0)	16067.215(0)
48.5	16001.580(1)	...	...	16068.350(−5)
49.5	16001.390(0)	...	...	...
50.5	16001.217(1)	...	...	...
51.5	16001.059(−0)	...	...	...
52.5	16000.918(−0)	...	...	...
53.5	16000.795(0)	...	...	...

[a] Units are cm^{-1}.
[b] Obs.-calc. in units of 10^{-3} cm^{-1} were computed with the constants of Table 2 and are given in parentheses.

TABLE 2

MOLECULAR CONSTANTS FOR THE CaOH $B\ ^2\Sigma^+$, $A\ ^2\Pi$, AND $X\ ^2\Sigma^+$ 000 STATES

Parameter[a]	$X\ ^2\Sigma^+$	$A\ ^2\Pi$	$B\ ^2\Sigma^+$
T_0	0.0	15998.128(1)	18022.268(1)
B_0	0.334354(8)	0.341428(8)	0.339409(10)
D_0	$3.869(24) \times 10^{-7}$	$3.919(27) \times 10^{-7}$	$3.707(100) \times 10^{-7}$
γ_0	0.00111	...	$-0.043615(46)$
p_0	...	$-0.042796(78)$	...
q_0	...	$-3.569(50) \times 10^{-4}$	...
A_0	...	66.795(1)	...
A_J	...	$2.126(71) \times 10^{-5}$	...

[a] Units are cm^{-1}, one σ uncertainty in parentheses.

TABLE 3

PREDICTED PURE ROTATIONAL TRANSITIONS OF CaOH

Transition $N+1 \to N$	Predicted Frequency[a] $F_1-F_1(e-e)$	$F_2-F_2(f-f)$
1–0	20064.	...
2–1	40111.	40078.
3–2	60158.	60124.
4–3	80203.	80170.
5–4	100248.	100215.
6–5	120291.	120258.
7–6	140333.	140300.
8–7	160372.	160340.
9–8	180410.	180377.
10–9	200445.	200412.

[a] In MHz.

sitions would permit a fairly secure identification of CaOH to be made.

IV. SUMMARY

Laser-based spectroscopic methods have allowed the rotational analysis of the electronic spectrum of CaOH. The ground state molecular constants provide useful predictions of the microwave transitions. The predicted microwave frequencies may facilitate the detection of CaOH in molecular clouds.

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PETER F. BERNATH and CHRIS R. BRAZIER: Department of Chemistry, University of Arizona, Tucson, AZ 85721