DYE LASER SPECTROSCOPY OF THE $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ TRANSITION OF CaOH

P.F. BERNATH and S. KINSEY-NIELSEN
Department of Chemistry, University of Arizona, Tucson, Arizona 85721, USA

Received 19 December 1983; in final form 6 February 1984

The $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ transition of CaOH has been examined by the technique of dye laser excitation spectroscopy. The rotational structure of the 000–000 and 100–100 bands was determined.

1. Introduction

When calcium salts are added to a flame, greenish and reddish emission from CaOH becomes prominent. These flame bands had been noted as early as 1823 by Herschel [1] but James and Sugden in 1955 [2] were the first to suggest CaOH as the carrier. The OH^- ligand is a pseudohalogen so the spectra strongly resemble the isoelectronic CaF. On this basis the red and green bands are assigned to the $A\,^2\Pi$–$X\,^2\Sigma^+$ and $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ transitions, respectively [2]. The B–X transition has also been tentatively identified in stellar spectra [3]

The experiments of Harris and co-workers [4–8] on alkaline earth hydroxides and amides demonstrated that substantial concentrations of polyatomic metal containing species can be generated with a Broida-type oven. As for the isoelectronic CaF, the congested bands of CaOH required a tunable dye laser in order to unravel the rotational structure. Hilborn et al. [7] analyzed the $A\,^2\Pi$–$X\,^2\Sigma^+$ transition of the linear CaOH. Although CaOH [7] and SrOH [5] were found to be linear, Trkula and Harris [8] found CuOH to be bent like the H_2O molecule.

The $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ transition of CaOH occurs in 5530–5570 Å region [2,4]. The X and B state potential curves are very similar so the band heads occur at high N. The presence of relatively low frequency Ca–O stretch (606 cm^{-1}) and Ca–O–H bend (339 cm^{-1}) [7] produces a large number of bands (with $\Delta v = 0$) in a relatively narrow wavelength region.

2. Method

The CaOH molecule was made in a Broida-type oven [9] by the reaction of Ca metal vapor with H_2O [4]. The calcium was evaporated from an alumina crucible and entrained in a flow of Ar carrier gas. The amount of CaOH produced could be enhanced by greatly decreasing the pumping speed until the total pressure in the oven (mostly Ar) was ≈9 Torr. The direct reaction to produce $X\,^2\Sigma^+$ CaOH,

$$Ca(g) + H_2O \rightarrow CaOH + H\,,$$

is endothermic by ≈19 kcal/mole ‡ (to produce the observed weak $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ chemiluminescence 70 kcal/mole are required!). For these reasons it is unlikely that the direct reaction is the major production pathway for CaOH.

The output of a Coherent 699-21 ring dye laser pumped by a 6 W from a Coherent Innova 20 argon ion laser was focused into the flame. The dye laser was operated near 5550 Å with rhodamine 110 dye. The resulting fluorescence was imaged onto the slits of a 0.64 m Instruments SA monochromator (HR-640) and detected by a cooled RCA C31034 photomultiplier tube with photon counting electronics.

By analogy with the SrOH $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ analysis of Nakagawa et al. [5] the 000–000 band was expected to be on the blue side of the chemiluminescent peak at 5560 Å. A few preliminary fluorescence scans were made by exciting a few strong features with the

‡ D_0^0(Ca–OH) = 92 ± 4 kcal/mole [10].

0 009-2614/84/$ 03.00

laser and examining the emitted light with a monochromator. This established whether the lines were P or R and provided an approximate N assignment. The data collection then proceeded by scanning the laser over 1 cm^{-1} segments in the P or R branch and detecting the fluorescence through the monochromator in the corresponding R or P branch. As has been described before [5,11,12] the monochromator acts as a filter to select only the lines of interest. In this case the lines of interest were in the 000–000 band but until the analysis was completed it was not certain which lines actually belonged to this band. Thus each 1 cm^{-1} scan was repeated 4 or 5 times with the monochromator set at a different wavelength. The slits of the monochromator were set to provide a bandpass of slightly more than 1 Å and the monochromator wavelength settings were 1 Å apart.

The scans were recorded with a two-pen chart recorder. The signal channel recorded the count rate from the photon counter while the calibration channel contained the I_2 excitation spectrum [13] and fringes from a 300 MHz Fabry–Pérot.

3. Results and discussion

The observed CaOH lines are listed in table 1. The estimated accuracy of the line positions is ±0.005 cm^{-1}. These line positions have been corrected by subtraction of 0.0056 cm^{-1} [14]. The assignments were made by first picking out the strongest two R series of lines and the strongest two P series. These were suspected of being R_1, R_2 and P_1, P_2 branches of the 000–000 band. Since CaOH resembles CaF quite closely the $A\,^2\Pi$ and $B\,^2\Sigma^+$ should form a unique perturber pair with $\gamma' \approx p' = -0.0437$ cm^{-1} [7] and $\gamma'' \approx 0.0013$ cm^{-1} [7]. Thus $R_1(N) - R_2(N) \approx P_1(N) - P_2(N) \approx \gamma' N = -0.0437N$ and the CaOH lines (like the CaF $B\,^2\Sigma^+ - X\,^2\Sigma^+$) were quickly assigned on this basis [12]. The ground-state combination differences were found to agree with those of Hilborn et al. [7] confirming that the transition originated from the 000 vibrational level. The excited state constants were very similar to the ground-state constants and we were presumably working in the $\Delta v = 0$ sequence so the vibrational assignment of the band had to be 000–000.

The remaining lines were assigned to two additional bands. Rotational assignments of these bands were made in the same way as for the 000–000 band. Unfortunately only a few R_1 and R_2 lines were observed for one of these bands (probably 200–200 vibrational band with origin ≈18018.2 cm^{-1}). The lines from the other band (assigned 100–100) are listed in table 1.

Each of the bands in table 1 was fit to the usual $^2\Sigma$ energy level expressions using a non-linear least-squares procedure [15]. The molecular constants from these fits are listed in table 2.

The ground-state molecular parameters are in reasonable agreement with those of Hilborn et al. [7]. Note that the ground-state spin rotation constant γ was fixed to 0.0013 cm^{-1} (the value for CaF [16]) since only $\gamma' - \gamma''$ is well determined for a $^2\Sigma$–$^2\Sigma$ transition. For the 100–100 band the D'' parameter was fixed at the value obtained in the 000–000 band fit. This was done because the unconstrained D' and D'' values were not well determined and seemed to be too large, probably because of the less extensive data set for this band.

The main evidence for the vibrational assignment of the 100–100 band rests on the size of the B'' value and the band origin. In SrOH when the metal–oxygen stretch (ν_1) is excited the band origin changes from 16377.505 cm^{-1} to 16383.890 cm^{-1} while the B values changes from 0.24921 cm^{-1} to 0.24772 cm^{-1} ($\alpha_1'' = 0.00149$ cm^{-1}) [5]. The corresponding values from the 010–010 band where the bend (ν_2) is excited are 16414.652 cm^{-1} and 0.24859 cm^{-1} ($\alpha_2'' = 0.00062$ cm^{-1}) [5]. If OH^- is treated as a single unit (pseudohalide) then $\alpha_{CaOH} \approx \alpha_{SrOH}(B_{CaOH}/B_{SrOH})^{3/2}$ since B scales as $1/\mu$ and α scales as $(1/\mu)^{3/2}$ for a diatomic [17]. The estimated α_1 and α_2 values on this basis for CaOH are thus 0.00232 cm^{-1} and 0.00096 cm^{-1}, respectively, compared to the observed $\alpha_1 = 0.00222$ cm^{-1}. In addition for SrOH the band origin changes by +6 cm^{-1} going from the 000–000 band to the 100–100 but +37 cm^{-1} to the 010–010. For CaOH the change in band origin from the 000–000 band to the 100–100 is –2 cm^{-1}. Thus our vibrational assignment of the 100–100 band is consistent with the secure SrOH assignments [5].

The rotational analysis presented in this paper allows some of the band heads reported in the literature to be assigned. The assignments are somewhat speculative since the band heads occur at high N

Table 1
The measured lines of the CaOH 000–000 and 100–100 $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ transition (in cm^{-1}). The numbers in parentheses are observed − calculated in units of 10^{-3} cm^{-1}

N	$P_1(N)$	$P_2(N)$	$R_1(N)$	$R_2(N)$
		000–000		
1				
2	18020.915(3)			
3	18020.241(0)	18020.355(0)		
4	18019.584(3)	18019.740(1)	18025.646(−1)	18025.892(1)
5	18018.931(0)	18019.135(1)	18026.351(−2)	18026.641(−1)
6	18018.290(−1)	18018.539(2)	18027 070(0)	18027.405(1)
7	18017.661(0)	18017 952(0)	18027 800(3)	18028.175(0)
8			18028.535(1)	18028.958(0)
9	18016.429(−2)	18016.811(−1)	18029.285(4)	18029.750(1)
10	18015.832(1)	18016.253(−4)	18030.038(0)	18030.548(−3)
11	18015.246(4)	18015.712(−1)	18030 801(−4)	18031.361(−1)
12		18015.179(0)	18031.581(−1)	18032.183(−2)
13	18014.090(−4)	18014 657(3)	18032.368(0)	18033.017(1)
14	18013.533(−3)	18014 136(−5)	18033.167(1)	18033.843(−3)
15	18012.985(−2)	18013.637(0)	18033.970(−2)	18034.711(3)
16	18012.453(3)	18013.141(−3)	18034.792(3)	18035.573(2)
17	18011.923(2)	18012.667(7)	18035.614(−2)	
18	18011.402(−2)	18012.190(2)		
19	18010.895(−2)	18011.725(0)		
20	18010.400(0)	18011.270(−3)		
21	18009.917(3)	18010.827(−4)		
22	18009.443(6)	18010.400(0)		
23	18008.976(5)	18009.975(−4)		
24	18008.512(−4)	18009.572(4)		
25	18008.065(−5)	18009.175(8)		
26		18008.783(5)		
27		18008 390(−8)		
		100–100		
3				
4				
5				
6	18016.714(0)		18025.429(0)	18025.765(0)
7	18016.086(1)		18026.147(−1)	18026.525(−3)
8	18015.466(0)		18026.884(8)	18027.301(0)
9	18014.855(−2)		18027.615(2)	18028.082(−1)
10	18014.257(0)		18028.359(0)	18028.878(3)
11			18029 120(4)	18029.675(−1)
12	18013.078(−9)		18029.880(−1)	18030.484(−3)
13	18012.527(10)	18013.078(−1)	18030.654(−2)	18031.305(−1)
14		18012.559(−4)	18031.438(−3)	18032.136(−1)
15	18011.403(−1)	18012.057(0)	18032.228(−6)	18032.983(8)
16		18011.555(−5)		
17	18010.333(2)	18011.069(−4)		
18	18009.815(7)	18010.590(−6)		
19	18009.301(5)	18010.133(5)		
20	18008.785(−7)	18009.675(5)		
21	18008.298(−1)	18009.226(5)		
22	18007.816(1)			
23	18007.335(−5)			
24	18006.876(1)	18007.928(−3)		
25		18007.522(1)		
26		18007.119(0)		

Table 2
The molecular constants of the $B\,^2\Sigma^+$–$X\,^2\Sigma^+$ CaOH transition (in cm^{-1})

	000–000	100–100
ν	18022 263(1) [a]	18020.666(2)
B'	0.339385(43)	0.336928(33)
D'	4.54(95) x 10^{-7}	5.16(23) x 10^{-7}
γ'	−0.043418(49)	−0.043624(83)
B''	0.334327(40)	0.332106(28)
D''	4.50(81) x 10^{-7}	4.5 x 10^{-7} [b]
γ''	0 0013 [c]	0.0013 [c]

a) One standard deviation uncertainty.
b) Fixed to the value for CaOH $X\,^2\Sigma^+$ 000 state.
c) Fixed to the value for CaF $X\,^2\Sigma^+$ state.

(>50) well beyond our region of observation. These heads are displayed weakly in flame spectra [18–20]. The bandheads at 5554.3 and 5553.4 Å are very likely to be the P_1 and P_2 (respectively) heads of the 000–000 band. The corresponding P_1 and P_2 heads of the 100–100 band might be at 5555.2 and 5554.3 Å (overlapped). By analogy with SrOH the pair of bands at 5547.4 and 5546.4 Å could belong to the 010–010 band, while the 020–020 could be 5543.0 and 5542 6 Å.

The correspondence between CaF and CaOH is very strong. Not only are the B and D constants similar, the $A\,^2\Pi$ and $B\,^2\Sigma^+$ states form a unique perturber pair [15] with $\gamma_0(-0.04342\ cm^{-1}) \approx p_0$ ($-0.04389\ cm^{-1}$). The pure precession value [21] for $l = 1$ has

$$p_0 \approx \gamma_0 = \frac{4A_0B_0}{E_0(A\,^2\Pi) - E_0(B\,^2\Sigma^+)} = -0.0451\ cm^{-1}$$

in reasonable agreement with the observed values. This does *not* imply that the A and B states come from a p orbital, but simply that $l_{effective} = 0.983$. It is possible for the $B\,^2\Sigma^+$ state to be a completely mixed pσ and dσ state and still have $l_{eff} = 1$ [22]. These similarities to CaF support the Ca^+OH^- picture of the electronic structure. The electronic transitions occur among atomic-like, metal-centered orbitals distorted by the OH^- ligand field.

Acknowledgement

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. This research was also supported by a grant from the National Science Foundation (CHE-8306504). We thank Leo Kenney for help with the data reduction.

References

[1] J.F.W. Herschel, Trans. Roy. Soc. (Edinburgh) 9 (1823) 445.
[2] C.G. James and T.M. Sugden, Nature 175 (1955) 333.
[3] P. Pesch, Astrophys. J. 174 (1972) L155.
[4] R.F. Wormsbecher, M. Trkula, C Martner, R.E Penn and D.O. Harris, J. Mol. Spectry. 97 (1983) 29.
[5] J. Nakagawa, R.F. Wormsbecher and D.O. Harris, J Mol. Spectry. 97 (1983) 37.
[6] R.F. Wormsbecher, R E. Penn and D.O. Harris, J. Mol. Spectry. 97 (1983) 65.
[7] R.C. Hilborn, Zhu Qingshi and D.O. Harris, J. Mol. Spectry. 97 (1983) 73.
[8] M. Trukula and D.O. Harris, J. Mol. Spectry. 97 (1983) 73.
[9] J.B. West, R.S. Bradford, J.D. Eversole and C.R Jones, Rev. Sci. Instrum. 46 (1975) 164.
[10] E. Murad, J. Chem. Phys. 75 (1981) 4080.
[11] C. Linton, J. Mol. Spectry. 69 (1978) 351.
[12] M. Dulick, P.F. Bernath and R.W. Field, Can. J. Phys. 58 (1980) 703.
[13] S. Gerstenkorn and P. Luc, Atlas du spectra d'absorption de la molecule d'iode (CNRS, Paris, 1978).
[14] S. Gerstenkorn and P. Luc, Rev. Phys. Appl. 14 (1979) 791.
[15] R.N. Zare, A.L Schmeltekopf, W.J. Harrop and D.L Albritton, J. Mol. Spectry. 46 (1973) 37.
[16] P.F. Bernath, P.G. Cummins and R.W. Field, Chem. Phys. Letters 70 (1980) 698.
[17] G Herzberg, Spectra of diatomic molecules, 2nd Ed (Van Nostrand, Princeton, 1950).
[18] R W.B. Pearse and A.G. Gaydon, The identification of molecular spectra, 4th Ed. (Chapman and Hall, London, 1976).
[19] S.J. Weeks, H. Haraguchi and J.D. Winfordner, J. Quant. Spectrosc. Radiat. Transfer 19 (1978) 633.
[20] J. van Hurk, Tj Hollander and C.Th.J. Alkemade, J. Quant. Spectrosc. Radiat. Transfer 13 (1973) 273.
[21] R.S. Mulliken and A. Christy, Phys. Rev. 38 (1931) 87.
[22] P.F. Bernath, Ph.D. Thesis, Massachusetts Institute of Technology (1980).