Laser Fluorescence Excitation Spectroscopy of CaOH and CaOD: The $A^2\Pi - X^2\Sigma^+$ (100)–(000) Band System and the (100)–(020) Fermi Resonance

JOHN A. COXON, MINGGUANG LI, AND PAUL I. PRESUNKA

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

The $A^2\Pi - X^2\Sigma^+$ (100)–(000) bands of the gas-phase CaOH and CaOD radicals have been rotationally analyzed by high-resolution laser spectroscopy. The $A^2\Pi_{3/2}$ component of the (100) level of CaOH and the $A^2\Pi_{1/2}$ component of the (100) level of CaOD are severely perturbed by the $A^2\Pi$ (020) level through Fermi resonance. Each of the four subbands of CaOH and CaOD has been fitted separately. Selective detection of laser-induced fluorescence has effectively enhanced and simplified the excitation spectra, and has facilitated the analysis of the perturbed subbands. © 1991 Academic Press, Inc.

I. INTRODUCTION

Although the well-known red-green emission of CaOH from flames containing calcium salts was first described (1) in 1823, the actual identity of the emitting species remained uncertain for many years. By analogy with the emission of the isoelectronic CaF radical, James and Sugden (2) suggested assignment of the red and green systems of CaOH as $A^2\Pi \rightarrow X^2\Sigma^+$ and $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transitions, respectively. However, an unequivocal assignment of the red system as an $A^2\Pi - X^2\Sigma^+$ transition, as well as the linear structure of CaOH, was established only as recently as 1983 by Hilborn *et al.* (3). Using a low-temperature (~700 K) Broida oven (4) as a source of CaOH, these authors used laser techniques to examine the vibrational structure of the $A^2\Pi$ and $X^2\Sigma^+$ states in some detail, and performed a rotational analysis of the A(000)-X(000) bands of both CaOH and CaOD.

The most recent work has been concerned with both the $B^2\Sigma^+ - X^2\Sigma^+$ and $A^2\Pi - X^2\Sigma^+$ transitions of CaOH; the rotational structure of the B-X (000)-(000) and (100)-(100) bands was analyzed by Bernath and co-worker (5) and by Li *et al.* (6). Li and co-workers (7) have extended the earlier rotational analysis of the A-X system of CaOH to include the $A^2\Pi_{1/2} - X^2\Sigma^+$ (100)-(000) subband. Ostensibly as the result of a Fermi resonance between the (100) and (020) levels of the $A^2\Pi$ state, the appearance and complexity of the (100)-(000) band is markedly different from that of the (000)-(000) band. Even without such complications, rotational analyses of the A-X and B-X transitions of CaOH and CaOD are not trivial undertakings, and much remains to be done. The low-lying states (as in CaF) involve promotion of a non-bonding electron located on the metal center, so that the shapes of potential energy curves of the X, A, and B states are closely similar. This leads to severely overlapped and congested spectra from strong $\Delta v = 0$ sequences.

In this paper, we present a more complete rotational analysis of the $A^2\Pi - X^2\Sigma^+$ band system for both the CaOH and CaOD isotopomers. The effect of the Fermi resonance on the (100) level, and the experimental methods used to distinguish the $\Delta v_1 = 1$ and $\Delta v_2 = 2$ transitions are described.

II. EXPERIMENTAL DETAILS

The CaOH/CaOD radicals were produced in a modified Broida-type oven (4). Briefly, calcium metal was vaporized in an alumina crucible, resistively heated by a tungsten wire basket. Metal vapor entrained in a flow of prepurified argon gas was carried into a fluorescence chamber where it was oxidized with either H_2O or D_2O . Typically, the oxidant partial pressure is a few mTorr at a total operating pressure of approximately 5 Torr. In later experiments, the presence of a microwave discharge (2450 MHz) through the H_2O/D_2O flow prior to reaction with Ca vapor was found to increase the S/N by about one order of magnitude. The output of a Coherent 699-29 single mode ring dye laser was directed vertically through the fluorescence chamber, parallel to the flow direction of the CaOH/CaOD radicals.

The laser-induced fluorescence (LIF) was monitored through two separate detection schemes. Total unresolved fluorescence was detected with a low grade photomultiplier in conjunction with a spatial filter and long pass cut-off filter. On the dispersive side, the LIF was focused onto the entrance slit of a 1.0-m Spex monochromator fitted with an RF-shielded GaAs photomultiplier (RCA C31034A). Phase sensitive detection with a modulation frequency of 540 Hz was used to suppress the unwanted chemiluminescence. Resolved fluorescence spectra, used for rotational assignment as well as the vibrational classification, were taken using a slit width of 0.1 mm (~1.0 Å resolution). In most cases this was sufficient to establish the rotational quantum number to within one of two possibilities. The monochromator was also used as a tunable band-pass filter (with slit width ~0.7 mm, spectral bandwidth ~7 Å) to selectively detect the LIF for excitation spectra. The primary advantage of the selective detection lay with the ability of this technique to simplify the appearance of the highly congested excitation spectrum.

Figure 1 depicts our experimental scheme, which is based on the vibrational analysis of Hilborn *et al.* (3). When $\Delta v_1 = +1$ and $\Delta v_2 = +2$ transitions are excited, $\Delta v_i = 0$ emissions are the dominant (>90%) component of the LIF. The vibrational term values for the (100) and (020) levels for the ground state of CaOH are 606 and 680 cm⁻¹, respectively. Consequently, by maintaining the monochromator at a frequency that is 606 (or 680) cm⁻¹ lower than the laser frequency, the $\Delta v_i = 0$ component of the LIF is selectively detected. In the present study, not only did this result in much simplified spectra and enhanced signal strengths, it also proved to be a valuable diagnostic tool. Both types of CaOH fluorescence excitation spectra were recorded in the spectral range 16 550–16 700 cm⁻¹. The $\Delta \bar{\nu} = 606$ cm⁻¹ spectrum covered the entire region while the $\Delta \bar{\nu} = 680$ cm⁻¹ spectrum was absent in the lower-frequency region. We were therefore able to quickly identify the unperturbed $A^2\Pi_{1/2} \rightarrow X^2\Sigma^+$ (100)–(000) subband at $\bar{\nu} < 16 633$ cm⁻¹. In the higher-frequency region, the same subbands were present in both spectra, indicating that the upper levels are mixed through perturbations; however, the *relative* intensities of individual subbands are



FIG. 1. Energy level diagram for the $A^2\Pi$ and $X^2\Sigma^+$ states of CaOH and CaOD, based on the vibrational analysis of Hilborn *et al.* (3), but with the (020)–(000) vibrational interval for CaOD determined in the present work; the positions of other experimentally unobserved CaOD bending levels have been adjusted accordingly. The selective detection scheme is shown in the diagram. The vibronic structures of the bending levels have not been experimentally determined; the (020) level is shown schematically in the inset.

different in the two spectra, and it was possible then to infer which bands corresponded to the $A^2\Pi_{3/2} - X^2\Sigma^+$ (100)–(000) or (020)–(000) transitions.

In the case of CaOD, the same region of the spectrum was examined using frequency differences of $\Delta \bar{\nu} = 603$ and 520 cm^{-1} . Our experiments have shown that the 240cm⁻¹ vibrational spacing of the CaOD ν_2 mode reported in Ref. (3) is unreliable. We have determined the spacing between the (020) and (000) levels in the X state to be $520 \pm 1 \text{ cm}^{-1}$ from resolved LIF spectra following excitation of rotational transitions of the A-X (100)-(000) band. This 520-cm⁻¹ interval corresponds to the term value of the $^2\Sigma$ component of the X(020) level; the $^2\Delta$ component is at slightly higher energy. A detailed vibrational analysis of the ground electronic state is now in progress in our laboratory. Strong Fermi resonance between the $A^2\Pi_{1/2}(100)$ and A(020)levels gave significant intensity to the LIF corresponding to the A(100)-X(020) transitions, as described in Section III. Since the (020) level lies lower in energy than (100) (see Fig. 1), the $\Delta \bar{\nu} = 520 \text{ cm}^{-1}$ spectrum exhibits structure only in the lower-

|--|

Observed Line Positions^a (cm⁻¹) for the $A^2\Pi - X^2\Sigma^+$ (100)-(000) Band of CaOH

	<i>Q</i> ₁		<i>R</i> ₁	R_1		
J	ν _{obs}	Δν	$\tilde{\nu}_{obs}$	Δν	$\overline{\nu}_{obs}$	Δī
1/2	16586.394	-0.003				
1½	86.714	-0.003			16585.767	0.005
21⁄2	87.035	-0.008			85.456	-0.012
31⁄2	87.366	-0.009			85.177	0.007
41⁄2	87.713	0.000			84.880	0.003
51⁄2	88.053	-0.003			84.594	0.004
6½	88.404	-0.001			84.312	0.003
71⁄2	88.761	0.001			84.028	-0.006
81⁄2	89.121	0.000			83.769	0.005
9½	89.488	0.000			83.505	0.006
10½	89.859	-0.002			83.247	0.006
11½	90.240	0.001	16599.207	-0.005	82.995	0.007
121⁄2	90.623	-0.001	600.305	-0.006	82.745	0.004
13½	91.009	-0.006	1.410	-0.007	82.505	0.006
14½	91.415	0.004	2.522	-0.005	82.271	0.008
15½	91.817	0.003	3.635	-0.008	82.032	-0.001
16½	92.227	0.004	4.763	-0.001	81.813	0.005
17½	92.636	-0.001	5.891	0.000	81.596	0.007
18½	93.057	-0.001	7.014	-0.008	81.378	0.003
19½	93.487	0.002	8.152	-0.007	81.177	0.009
201⁄2	93.920	0.001	9.304	0.002	80.973	0.008
211⁄2	94.357	-0.001	10.442	-0.007	80.780	0.011
221⁄2	94.804	0.000	11.592	-0.010	80.590	0.012
231⁄2	95.258	0.002	12.752	-0.008	80.400	0.007
24½	95.706	-0.008	13.920	-0.003	80.223	0.010
25½	96.180	0.001	15.086	-0.005	80.048	0.009
261⁄2	96.651	0.001	16.263	-0.001	79.884	0.013
271⁄2	97.122	-0.005	17.437	-0.005	79.710	0.001
281⁄2	97.610	-0.001	18.620	-0.006	79.560	0.008
29½	98.105	0.004	19.808	-0.006	79.400	-0.001
30½	98.603	0.006	21.010	0.002	79.256	0.001
311⁄2	99.101	0.001	22.191	-0.015	79.113	-0.003
321⁄2	99.612	0.002	23.398	-0.012	78.986	0.004
331⁄2	600.123	-0.003	24.610	-0.009	78.853	-0.001
34½	0.649	0.000	25.824	-0.008	78.729	-0.002
351⁄2	1.175	-0.004	27.046	-0:005	78.616	0.001
36½	1.716	0.001	28.275	0.001	78.502	-0.002
371/2	2.258	0.000	29.503	0.001	78.396	-0.003
381/2	2.809	0.001	30.740	0.004		
391/2	3.362	-0.002	31.984	0.010		
401/2	3.929	0.002	33.230	0.013		
411/2	4.504	0.007				
42%	5.071	-0.003				
4,372	5.002	0.004				
4472	0.200	0.000				

 $\overline{{}^{a}\Delta\overline{\nu}}$ is the residual, $\overline{\nu}_{obs} - \overline{\nu}_{calc}$

TABL	E I—	Conti	nued

	<i>Q</i> ₁		<i>R</i> ₁		P ₁	
J	vobs	$\Delta \overline{\nu}$	v _{obs}	$\Delta \overline{\nu}$	$\overline{\nu}_{obs}$	$\Delta \overline{\nu}$
451/2	6.846	0.000				
46½	7.452	0.001				
47½	8.061	-0.002				
481⁄2	8.682	0.000				
49½	9.304	-0.004				
50½	9.941	0.000				
511/2	10.580	-0.001				
52½	11.228	0.000				
53½	11.879	-0.003				
54½	12.538	-0.006				
55%	13.210	-0.003				
56½	13.897	0.008				
·	Q ₂		R ₂		P ₂	
J	$\bar{\nu}_{obs}$	$\Delta \overline{\nu}$	$\bar{\nu}_{obs}$	$\Delta \overline{\nu}$	$\bar{\nu}_{obs}$	$\Delta \overline{\nu}$
11/2	16643.693	-0.009				
21⁄2	43.390	0.009				
31/2	43.065	-0.001				
41/2	42.750	-0.007				
51/2	42.452	0.000	16646.829	-0.008		
61/2	42.146	-0.007	47 207	-0.007		
7%	41 857	-0.003	47 589	-0.007		
81/2	41 568	-0.003	47.987	-0.007		
91/2	41.500	-0.001	48 376	-0.002		
10%	41.012	0.001	48.578	-0.002		
11%	40 741	0.005	49.178	-0.005		
121/2	40.477	0.009	49.593	-0.003	16632 075	0.009
131/2	40.711	0.005	50.014	0.001	31 1/8	0.000
141/2	30 054	0.000	50.431	-0.003	30,210	-0.002
151/2	30 704	0.000	50.860	-0.003	20.210	-0.002
161/2	30 / 58	0.009	51 200	-0.005	29.290	0.004
171/2	30 214	0.011	51 732	-0.009	20.300	0.000
1814	39.214	0.010	52 183	-0.006	21.479	0.003
101/2	28 747	0.010	52.165	-0.004	20.307	-0.010
201/2	38 515	0.015	52.041	-0.000	20.000	-0.002
2072	20.013	0.009	53.U95 53.E95	-0.005	24.796	-0.002
21/2 2214	J0.204	0.000	33.303	~0.001	23.918	0.000
2272	38.074	0.008	54.028	-0.011	23.041	-0.004
2372 2414	37.804	0.001	54.504	-0.013	22,172	-0.006
2472	37.030	0.003	55,000	-0.002	21.321	0.002
2372	37.443	0.003	55.486	-0.008	20.472	0.006
20% 2714	57.242	-0.002	55.990	~0.002	19.621	0.001
2172 2814	37.040	-0.004	20.490	0.000	18.804	0.024
2072 2014	30.834	-0.008	57.004	-0.003	17.956	0.008
4772 2014	30.0/0	-0.002	57.523	-0.002	17.133	0.001
311/2	30.492	~0.007 -0.004	58.U56 50 507	0.007		
3172 2014	26 140	-0.000	28.286	0.006		
5472	30.148	~0.008				

	\mathcal{Q}_2		R ₂		P ₂	
J	$\bar{\nu}_{obs}$	$\Delta \overline{\nu}$	$\overline{\nu}_{obs}$	$\Delta \overline{\nu}$	$\overline{\nu}_{obs}$	$\Delta \overline{\nu}$
331⁄2	35.989	-0.002				
34½	35.833	0.001				
351⁄2	35.677	0.000				
361⁄2	35.519	-0.008				
371⁄2	35.384	0.003				
381⁄2	35.251	0.010				

TABLE I-Continued

frequency region. The $A^2 \Pi_{3/2} - X^2 \Sigma^+$ (100)–(000) subband appearing in the higherfrequency region of the $\Delta \bar{\nu} = 603 \text{ cm}^{-1}$ spectrum was readily identified.

Line positions were measured using the internal wavemeter of the CR 699-29 laser. For the LIF excitation spectra of CaOH and CaOD, I_2 fluorescence excitation spectra (8) were recorded simultaneously and where necessary small corrections were applied. The Doppler broadened width of the CaOH/CaOD lines was approximately 0.04 cm⁻¹ (FWHM); the estimated uncertainty of the measured line positions is 0.005 cm⁻¹.

III. ROTATIONAL ANALYSIS AND DISCUSSION

As for the (000)-(000) bands, the (100)-(000) bands of CaOH and CaOD show the same structure as for a Hund's case (a) ${}^{2}\Pi - {}^{2}\Sigma$ band of a diatomic molecule. For $A^{2}\Pi$, A/B = 196 and 213 for CaOH and CaOD, respectively. Although the two sub-



FIG. 2. Resolved LIF spectrum obtained from excitation of the $Q_2(12\frac{1}{2})$ transition in the CaOH $A^2\Pi_{3/2}(100) - X^2\Sigma^+(000)$ subband. The portion of the spectrum near the laser frequency is not shown. The frequency of the $(Q_2 + P_{21})$ line is ~606 cm⁻¹ lower than the laser excitation frequency. The occurrence of the A(100) - X(020) LIF lines is due to the (100) - (020) mixing in the upper level.

bands each contain six branches, spin-rotation splittings in the ground state are so small ($\gamma'' = 0.00111 \text{ cm}^{-1}(9)$) that the two Q branches are essentially coincident with a P branch and an R branch. Among the four observable branches in each subband, the intensities of the (Q + P) and (Q + R) composite branches were approximately twice those of the branches containing single resolved lines; this was an important feature of the spectra in terms of pattern recognition. Individual rotational lines were approximately the product of the spectra in terms of pattern recognition.

feature of the spectra in terms of pattern recognition. Individual rotational lines were assigned by analysis of resolved LIF spectra in the longer wavelength ($\Delta v_1 = 0$) region. (The $\Delta v_1 = 1$ fluorescence near the laser frequency was weak and overwhelmed by scattered laser light.) Such LIF spectra showed two peaks, corresponding to (P + Q)and R, or P and (Q + R) lines. We assigned the rotational quantum numbers by measuring the P - R separations. Two criteria were established in analyzing the resolved spectra: first, if a P line was excited, the fluorescence line at longer wavelength must have a 606-cm⁻¹ frequency difference from the laser excitation for the CaOH (100)-(000) band; similarly, if an R line was excited, the shorter wavelength line must have the 606-cm⁻¹ difference. Second, one peak should be approximately twice the intensity of the other, with this intensity pattern being consistent with the particular combination, Q + P or Q + R. In practice, there were more than two peaks in each spectrum due to coincident excitations. By application of the two criteria, we were able to rule out such irrelevant lines. For a relatively unperturbed subband, measuring P - R separations for six or seven rotational lines belonging to two or three branches was found sufficient for the numbering to be established unequivocally. However, for a subband in which the upper ${}^{2}\Pi_{1/2}$ or ${}^{2}\Pi_{3/2}$ spin-orbit component was perturbed through Fermi resonance with the (020) level, both the intensity pattern and the molecular constants are distorted; a large number of resolved LIF spectra were then required for the assignments.

For CaOH, the $A^2\Pi_{1/2}(100)$ level is estimated to lie approximately 70 cm⁻¹ below the $A(020)\mu^2\Pi_{1/2}$ vibronic level. The $A^2\Pi_{1/2}(100)-X^2\Sigma^+(000)$ subband was intense, and showed the expected structure for a ${}^2\Pi(a)-{}^2\Sigma$ transition; in addition, the resolved LIF spectra showed no lines corresponding to transitions to $X^2\Sigma^+(020)$ levels. We conclude then that there is no observable effect of Fermi resonance, to the sensitivity of our experiment, on the $A^2\Pi_{1/2}(100)$ level. (The same conclusion would be valid also for the $X^2\Sigma^+(100)$ level.) The 124 line positions measured for the $A^2\Pi_{1/2}(100)-X^2\Sigma^+(000)$ subband of CaOH are listed in Table I. These data are obtained with somewhat better accuracy than in the previous study of Li and co-workers (7); in addition, data are obtained for 28 newly assigned lines.

The CaOH $A^2\Pi_{3/2}(100)$ level, as shown in Fig. 1. is nearly degenerate with the lower vibronic components of the $A^2\Pi(020)$ level. A strong Fermi resonance between the (100) and (020) levels is expected. Our rotational analysis locates the ${}^2\Pi_{3/2}(100)$ level at 16 644.4 cm⁻¹, which is 7.9 cm⁻¹ lower than its unperturbed position if we assume the spin-orbit splitting of the (100) level to be the same as that of the (000) level in the $A^2\Pi$ state. The intensity of the $A^2\Pi_{3/2}(100)-X^2\Sigma^+(000)$ subband is obviously lower than that of the $A^2\Pi_{1/2}(100)-X^2\Sigma^+(000)$ subband. This can be readily attributed to transition strength borrowing by the $A^2\Pi(020)-X^2\Sigma^+(000)$ transition. The $\Delta v_2 = 2$ transitions are weaker by approximately two orders than the $\Delta v_1 = 1$ transitions from our observations, which is also in agreement with the observations in Ref. (3). Figure 2 shows a resolved LIF spectrum obtained from excitation

TABLE II

Observed Line Positions^a (cm⁻¹) for the $A^2\Pi - X^2\Sigma^+$ (100)–(000) Band of CaOD

	Q ₁		R _i		<i>P</i> ₁	
J	vobs	Δν	ν obs	$\Delta \vec{\nu}$	ν _{obs}	$\Delta \overline{\nu}$
31/2					16579.773	0.003
41⁄2					79.550	-0.002
51⁄2	16582.583	0.013			79.327	-0.015
6½	82.961	-0.004			79.128	-0.010
7½	83.360	-0.005			78.934	-0.007
81⁄2	83.770	0.000			78.744	~0.008
91⁄2	84.181	0.001			78.568	-0.001
10½	84.587	-0.009			78.394	0.001
111/2	85.017	0.000			78.225	0.001
121⁄2	85.438	-0.005			78.068	0.007
131⁄2	85.872	-0.002	16595.181	0.008	77.913	0.007
14½	86.301	-0.010	96.248	0.002	77.759	0.003
15½	86.748	-0.005	97.311	-0.014	77.623	0.010
16½	87.206	0.005	98.409	-0.001	77.480	0.004
171⁄2	87.661	0.007	99.512	0.012	77.347	0.002
18½	88.115	0.003	0.598	0.002	77.225	0.004
19½	88.583	0.008	1.693	-0.005	77.100	-0.002
201⁄2	89.053	0.009	2.802	-0.002	76.986	-0.003
211/2	89.538	0.020	3.904	-0.011	76.884	0.002
221/2	89.998	0.000	5.025	-0.006	76.786	0.007
231/2	90.484	0.001	6.154	0.002	76.679	-0.004
241⁄2	91.060	-0.014	7.276	-0.001	76.581	-0.010
251/2	91.459	-0.011	8.412	0.006	76.504	0.000
261/2	91.966	-0.006	9.548	0.008	76.434	0.012
271/2	92.479	0.000	10.674	-0.003		
281/2	92,987	-0.005	11.810	-0.007		
2016	93 514	0.004	12,956	-0.005		
301/2	94 034	0.000	14 099	-0.009		
311/2	94 558	-0.006	15 264	0.005		
321/2	95 111	0.000	16 4 18	0.007		
331/2	95.461	-0.001	10.110	0.007		
	Q_2	L.	R2		P ₂	
J	vobs	$\Delta \overline{\nu}$	$\overline{\nu}_{obs}$	$\Delta \overline{\nu}$	$\overline{\nu}_{obs}$	$\Delta \overline{\nu}$
1/2			16648.632	0.008	<u></u>	
11/2	16647.418	0.005	48.960	0.005		
21/2	47.139	0.000	49.299	0.002		
31/2	46.872	-0.003	49.652	0.003		
4½	46.627	0.005	50.016	0.003		
5½	46.384	0.004	50.387	0.000		
6½	46.148	-0.001	50.775	0.002		
71⁄2	45.931	0.001	51.164	-0.005	16641.307	0.003
8½	45.724	0.003	51.571	-0.005	40.480	0.002
91⁄2	45.525	0.002	51.991	-0.002	39.661	-0.002

 ${}^{a}\Delta\overline{\nu}$ is the residual, $\overline{\nu}_{obs} - \overline{\nu}_{calc}$

		Т	ABLE II—Co	ntinued			
	<i>Q</i> ₂		R ₂	R ₂		P ₂	
J	$\bar{\nu}_{obs}$	$\Delta \overline{\nu}$	$\bar{\nu}_{obs}$	$\Delta \overline{\nu}$	$\overline{\nu}_{obs}$	$\Delta \overline{\nu}$	
101/2	45.339	0.002	52.418	-0.004	38.857	-0.002	
11½	45.169	0.008	52.855	-0.006	38.060	-0.006	
121⁄2	44.999	0.002	53.317	0.006	37.284	0.000	
13½	44.835	-0.008	53.767	-0.005	36.512	-0.001	
141/2	44.703	0.002	54.233	-0.010	35.749	-0.004	
151⁄2	44.573	0.003	54.723	-0.002	34.997	-0.007	
16½	44.450	0.000	55.213	-0.005	34.262	-0.004	
171/2	44.343	0.002	55.721	0.000	33.537	-0.001	
181⁄2	44.252	0.009	56.234	-0.001	32.817	-0.005	
191⁄2			56.759	-0.001	32.120	0.004	
201⁄2			57.293	-0.002	31.418	-0.003	
211/2			57.834	-0.007	30.734	-0.004	
221/2			58.394	-0.003	30.062	-0.003	
231/2			58.969	0.006	29.396	-0.007	
241⁄2			59.538	-0.002	28.752	0.001	
251/2			60.130	0.002	28.115	0.004	
261/2	band	l head	60.724	-0.001	27.484	0.003	
271⁄2			61.322	-0.011	26.868	0.006	
281⁄2			61.968	0.016	26.258	0.004	
29½			62.589	0.009	25.661	0.004	
301/2			63.216	-0.003	25.060	-0.011	
311/2			63.865	-0.003	24.496	0.001	
321/2					23.931	0.001	
331⁄2					23.375	0.000	
34½					22.836	0.004	
351⁄2					22.301	0.002	
36½					21.775	-0.002	
37½					21.267	0.002	
38½					20.769	0.005	
391/2					20.275	0.002	
40½	44.895	-0.001			19.795	0.002	
41½	45.055	0.002			19.322	-0.002	
421/2	45.225	0.005			18.871	0.006	
43½	45.399	0,001			18.414	-0.003	
44½	45.589	0.002			17.973	-0.006	
451⁄2	45.784	-0.003			17.545	-0.006	
461/2	45.994	-0.003			17.128	-0.006	
47½	46.225	0.006			16.725	-0.002	
48½	46.451	0.001			16.322	-0.009	
49½	46.692	-0.001			15.947	0.003	
501/2	46.943	-0.003			15.581	0.013	
511/2	47.209	-0.001			15.203	0.000	
521/2	47.485	0.001					
531/2	47.766	-0.003					
541/2	48.062	-0.003					
551/2	48.372	0.002					
571/2	48.683	-0.003					
511/2	49.011	-0.002					
38%2	49.355	0.006					

TABLE III

Effective Molecular Constants^a for the $A^2\Pi(100)$ and $X^2\Sigma^+(000)$ States of CaOH and CaOD

		A ² Π (100)				
	CaOH	CaO	D			
T ⁽¹⁾	16586.167(1)	16580.528(7) ^b	16580.390(16) ^c			
T ⁽²⁾	16644.442(2)	16648.0	073(1)			
B ⁽¹⁾	0.337221(5)	0.306326(55) ^b	0.30551(11) ^c			
$B^{(2)}$	0.337071(7)	0.3083	40(39)			
$D^{(1)}$	$3.502(42) \times 10^{-7}$	$5.87(23) \times 10^{-7}$	^b 2.57(40) \times 10 ^{-7 c}			
$D^{(2)}$	$3.601(53) \times 10^{-7}$	2.96(30	$(1) \times 10^{-7}$			
H ⁽¹⁾	$-1.97(43) \times 10^{-11}$	-	,			
$H^{(2)}$	-	$-1.63(76) \times 10^{-11}$				
Р	-0.04452(11)	-0.1265(25) ^b	0.1155(53) ^c			
P.	$6.055(94) \times 10^{-6}$	-				
ø	$5.751(47) \times 10^{-6}$	-1.631(3	38) × 10 ⁻⁶			
. <u></u>		$X^{2}\Sigma^{+}$ (000)				
B	[0.334354]	0.3028	59(37)			
D	$[3.869 \times 10^{-7}]$	2.73(2	9) \times 10 ⁻⁷			
H	$-1.83(42) \times 10^{-11}$	$-1.41(76) \times 10^{-11}$				
γ	[0.00111]	[0.00111]				
All v	alues are in cm ⁻¹ ; v	values in parentheses	s are 10 standard			

"All values are in cm⁻; values in parentheses are 1 σ standard deviations in units of the last significant digit of the corresponding constant; constants fixed at the values in Ref. (9) are indicated by square brackets. The parameters P and Q are defined by $P_v = p_v + 2q_v$ and $Q_v = \frac{1}{2}p_v (B_v/A_v)^2 + q_v B_v/A_v$, see text. ^bDerived from P_1 and R_1 branches.

^cDerived from the Q_1 branch.

of the $Q_2(12\frac{1}{2})$ rotational transition in the $A^2\Pi_{3/2}(100)-X^2\Sigma^+(000)$ subband. Two groups of lines were observed, and are separated by ~80 cm⁻¹, corresponding to the wavenumber difference between the (100) and (020) levels in the ${}^{2}\Sigma^+$ ground electronic state. In the shorter wavelength group, the two strong lines are $(Q_2 + P_{21})$ and R_{21} of the A(100)-X(100) transition. Two extra lines appearing in this group are due to an overlapped excitation. The lines in the longer wavelength group, which corresponds to the A(100)-X(020) transition, appear to be almost as intense as those in the first group, indicating that the $A^2\Pi_{3/2}(100)$ level is, in fact, essentially an equal mixture of the (100) and (020) levels. As mentioned before, the resolved LIF spectra from excitation of the $A^2\Pi_{1/2}(100)-X^2\Sigma^+(000)$ transitions show no peaks in the wavelength region of the (100)-(020) group. This confirms the conclusion that the spectrum shown in Fig. 2 arises entirely from (100) + (020) mixing in the upper level. The 83 measured rotational lines of this subband are listed in Table I.

The A(100)-X(000) band of CaOD is quite different from that of CaOH; by comparison, the A(000)-X(000) bands of CaOH and CaOD differ only by small isotope

shifts. Owing to the large mass of Ca compared to H and D, the bending vibration of the molecule can be described as essentially the motion of the H or D atom relative to the Ca–O bond axis. As a consequence, the bending frequency of CaOD is smaller by ~80 cm⁻¹ than that of CaOH. As shown in Fig. 1, the (020) level in the $X^2\Sigma^+$ state is ~74 cm⁻¹ higher than the (100) level for CaOH, while for CaOD, (020) is ~83 cm⁻¹ lower than the (100) level. A similar situation is expected for the $A^2\Pi$ state due to the nonbonding electronic character of the transition. This difference in bending frequencies is responsible for the different (100)–(020) Fermi resonance patterns of CaOH and CaOD. In CaOD, the $A^2\Pi_{3/2}(100)$ level is well separated from the (020) level and is not subject, therefore, to any observable Fermi resonance effect. Accordingly, the excitation spectrum of the $A^2\Pi_{3/2}(100)-X^2\Sigma^+(000)$ subband appears with undiminished intensity and regular structure. The 114 rotational lines assigned for this subband are listed in Table II.

The $A^2\Pi_{1/2}(100)$ level of CaOD is estimated to lie just a few wavenumbers (cm⁻¹) above the $A(020) \kappa^2\Pi_{1/2}$ vibronic level. The resolved LIF spectra indicate that the ${}^2\Pi_{1/2}(100)$ level is mixed with a large fraction (~20-40%) of (020) character through Fermi resonance. As a consequence, the transition strength of the $A^2\Pi_{1/2}(100)$ - $X^2\Sigma^+(000)$ subband is significantly reduced. Another almost equally intense band appears in the same spectral region, and is most probably the A(110)-X(010) subband. The X(010) level of CaOD is ~260 cm⁻¹ above the (000) level, and has significant population. The $(P_1 + Q_{12})$ branch of the $A^2\Pi_{1/2}(100)-X^2\Sigma^+(000)$ subband forms a head at 16 576.0 cm⁻¹, and is readily recognized. The $(Q_1 + R_{12})$ branch of this subband is also relatively strong; however, the R_1 branch is much weaker and largely blended. A total of 73 measured line positions of this subband are listed in Table II.

A weighted, nonlinear least-squares fitting procedure was used to fit each of the subbands separately. The $A^2\Pi$ case (a) levels were represented by the expressions (10-12)

$$F_{1}(J,_{f}^{e}) = T_{v}^{(1)} + B_{v}^{(1)}J(J+1) - D_{v}^{(1)}J^{2}(J+1)^{2} + H_{v}^{(1)}J^{3}(J+1)^{3}$$

$$\mp \frac{1}{2}P_{v}(J+\frac{1}{2}) \mp \frac{1}{2}P_{Dv}J(J+1)(J+\frac{1}{2}\mp 1) \quad (1)$$

$$F_{2}(J,_{f}^{e}) = T_{v}^{(2)} + B_{v}^{(2)}J(J+1) - D_{v}^{(2)}J^{2}(J+1)^{2} + H_{v}^{(2)}J^{3}(J+1)^{3}$$

$$\mp Q_{v}(J-\frac{1}{2})(J+\frac{1}{2})(J+\frac{3}{2}). \quad (2)$$

The usual expressions,

$$F(J,f) = B_v X - D_v X^2 + H_v X^3 \pm \frac{1}{2} \gamma_v (J + \frac{1}{2} \mp 1), \qquad (3)$$

where

$$X = (J + \frac{1}{2} \mp 1)(J + \frac{1}{2})$$
(4)

were employed for the ${}^{2}\Sigma^{+}$ state. Two sets of effective molecular constants, $T_{v}^{(1)}$ and $T_{v}^{(2)}$, $B_{v}^{(1)}$ and $B_{v}^{(2)}$, etc., were employed to express the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ spin-orbit components separately; this is necessary because of the significant perturbation of one of the two components through Fermi resonance with the (020) level. It is possible to include both spin-orbit components in a single Hamiltonian only when a full deperturbation of the (100)-(020) interaction is achieved. In the absence of a Fermi

resonance interaction, the parameters P_{ν} and Q_{ν} would have their conventional definitions, $P_{\nu} = p_{\nu} + 2q_{\nu}$ and $Q_{\nu} = (B_{\nu}/A_{\nu})(q_{\nu} + \frac{1}{2}p_{\nu}B_{\nu}/A_{\nu})$; $P_{D\nu}$ is an effective parameter which includes the centrifugal distortion correction to P_{ν} . For the fits of the unperturbed CaOH $A^{2}\Pi_{1/2}(100) - X(000)$ and CaOD $A^{2}\Pi_{3/2}(100) - X(000)$ subbands, the variances were $\hat{\sigma}^{2} = (1.14)^{2}$ and $(0.95)^{2}$, respectively, in accord with the estimated measurement error (0.005 cm^{-1}) . For the perturbed subbands, however, the variances were somewhat larger, $\hat{\sigma}^{2} \sim (1.4)^{2}$, indicating that the model of Eqs. (1) and (2) for A(100) levels perturbed through Fermi resonance is slightly inadequate. The fitted values of the constants are listed in Table III.

The constants for the $X^2\Sigma^+(000)$ level of CaOH were held fixed at the values obtained by Bernath and Brazier (9); these authors combined data from the $A^2\Pi(000)$ – $X^2\Sigma^+(000)$ and $B^2\Sigma^+(000)-X^2\Sigma^+(000)$ transitions in a merged least-squares fit with directly measured spin-rotation splittings for four high-*J* lines. Since the CaOH $A^2\Pi_{1/2}(100)$ level is relatively unperturbed, the fitted constants for this level can be combined with those for the (000) level in Ref. (3) to obtain a well-determined estimate of the vibrational spacing between G(100) and G(000) of the $A^2\Pi$ state, $\Delta G = 621.371$ cm⁻¹. This result is based on the usually accurate assumption that these two vibrational levels have the same spin-orbit splitting. The rotational constant $B_{[v]}$ for a linear triatomic molecule is given (13) by

$$B_{[v]} = B_e - \sum_i \alpha_i (v_i + \frac{1}{2}d_i) + \cdots$$
 (5)

Taking $B_0^{(1)} = 0.339796$ cm⁻¹ for ${}^{2}\Pi_{1/2}(000)$ from Ref. (3) and $B_1^{(1)} = 0.337221$ cm⁻¹ for ${}^{2}\Pi_{1/2}(100)$ from Table III, we obtain a fairly reliable estimate of α_1 for the ν_1 mode of 2.575 × 10⁻³ cm⁻¹. This value is very close to the value of $\alpha = 2.529 \times 10^{-3}$ cm⁻¹ for CaF, which was used by Hilborn *et al.* to determine the equilibrium rotational constant B_e . Let us assume that the $A^{2}\Pi$ and $B^{2}\Sigma^{+}$ states form a unique perturber pair and satisfy Van Vleck's pure precession hypothesis. The Λ -doubling constant p_{ν} is then given (14) by

$$p_v = 2A_v B_v l(l+1) / \Delta E(v).$$
(6)

Using the constants determined in this work and in Refs. (5, 9), $A_1 = 66.795 \text{ cm}^{-1}$, $B_1 = B_0 - \alpha_1 = 0.338773 \text{ cm}^{-1}$, $l_{\text{eff.}} = 1$, and $\Delta E(v) = E_{A(100)} - E_{B(100)} = -2007.24 \text{ cm}^{-1}$, we can then obtain $p_v = -0.0451 \text{ cm}^{-1}$, which is in excellent agreement with the value obtained from the fit, $p_v \approx -0.04452(11) \text{ cm}^{-1}$. The values of the fitted constants for the CaOH ${}^2\Pi_{3/2}(100)$ level indicate that the near degeneracy between the (100) and (020) levels introduces a large contribution from high-order Coriolis interactions to the rotational structure: the value of $B_v^{(2)}$ is much smaller than its expected value, $B_0^{(2)} - \alpha_1 = 0.340325 \text{ cm}^{-1}$; and Q_1 has a positive value which means the *e*-levels are lower in energy than the *f*-levels. In the unperturbed CaOD ${}^2\Pi_{3/2}(100)$ level, the opposite is found, namely, the *e*-levels are higher than the *f*-levels.

A large number of rotational lines have been measured for the well-behaved CaOD $A^2\Pi_{3/2}(100) - X^2\Sigma^+(000)$ subband. We believe the fitted constants for the CaOD $X^2\Sigma^+(000)$ state in Table III should be more accurate than those in Ref. (3). When the $A^2\Pi_{1/2}(100) - X^2\Sigma^+(000)$ subband was fitted, the constants of the ground state were fixed at the above values. However, attempts to fit all the data simultaneously

were not successful, and satisfactory fits were obtained only when the Q_1 branch was fitted separately from the P_1 and R_1 branches. The two sets of parameter values obtained in this way for the *f*- and *e*-levels, respectively, of ${}^2\Pi_{1/2}(100)$ are listed in Table III. The two separate estimates of p_v are both anomalously large and indicate that both the *e*- and *f*-levels of $A^2\Pi_{1/2}(100)$ are displaced upward by perturbations; however, they cannot be accommodated in the same fit by a larger effective B_v value. We expect that this complex rotational structure can only be interpreted satisfactorily through a full deperturbation from the (100)–(020) Fermi resonance.

In conclusion, it can be noted that although the (100)-(020) Fermi resonance renders the A(100)-X(000) band very complex and difficult to analyze, it nevertheless provides a convenient window for access to the excited bending vibrational levels. By exciting the extensive range of perturbed rotational levels in the $A^2\Pi$ state, which have been assigned in the present work, it will be possible to investigate the vibrational and rotational structure of the ground state excited bending mode, as well as the excited stretching mode, through resolved LIF spectra. Detailed vibrational and rotational information for the ground state will in turn greatly facilitate the analysis of the $A^2\Pi$ excited bending levels, and hence permit a full deperturbation for the (100)-(020) (and possibly the (110)-(030)) Fermi resonance in the A state. Such experiments are in progress in this laboratory.

ACKNOWLEDGMENTS

Support for this work from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. P.I.P. thanks Dalhousie University for the award of a Dalhousie Graduate Scholarship. Professor R. W. Field and Dr. J. Murphy (Massachusetts Institute of Technology) are thanked for their encouragement and for guidance in the design of the Broida oven.

RECEIVED: June 13, 1991

REFERENCES

- 1. J. F. W. HERSCHEL, Trans. R. Soc. Edinburgh 9, 445-460 (1823).
- 2. C. G. JAMES AND T. M. SUGDEN, Nature 175, 333-334 (1955).
- 3. R. C. HILBORN, Q. ZHU, AND D. O. HARRIS, J. Mol. Spectrosc. 97, 73-91 (1983).
- 4. J. B. WEST, R. S. BRADFORD, JR., J. D. EVERSOLE, AND C. R. JONES, *Rev. Sci. Instrum.* 46, 164–168 (1975).
- 5. P. F. BERNATH AND S. KINSEY-NIELSEN, Chem. Phys. Lett. 105, 663-666 (1984).
- 6. M. LI, Y. ZHANG, C. WANG, AND Q. ZHU, Appl. Laser 4, 149-152 (1984).
- 7. Q. ZHU, M. LI, Y. ZHANG, AND C. WANG, Acta Opt. Sin. 5, 765-768 (1985).
- S. GERSTENKORN AND P. LUC, "Atlas du Spectre d'Absorption de la Molecule d'Iode," Laboratoire Aimé-Cotton, CNRS II—91405 Orsay, France.
- 9. P. F. BERNATH AND C. R. BRAZIER, Astrophys. J. 288, 373-376 (1985).
- 10. G. HERZBERG, "Spectra of Diatomic Molecules," 2nd ed., Van Nostrand, New York, 1950.
- 11. R. S. MULLIKEN AND A. CHRISTY, Phys. Rev. 38, 87-119 (1931).
- 12. A. J. KOTLAR, R. W. FIELD, J. I. STEINFELD, AND J. A. COXON, J. Mol. Spectrosc. 80, 86–108 (1980).
- 13. G. HERZBERG, "The Spectra and Structures of Simple Free Radicals," p. 94, Cornell Univ. Press, 1971.
- 14. R. N. ZARE, A. L. SCHMELTEKOPF, W. J. HARROP, AND D. L. ALBRITTON, J. Mol. Spectrosc. 46, 37–66 (1973).