

INTERMODULATED FLUORESCENCE SPECTROSCOPY OF CaF A $^2\Pi-X^2\Sigma^+$ P.F. BERNATH, P.G. CUMMINS[‡] and R.W. FIELD*Spectroscopy Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

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The A $^2\Pi-X^2\Sigma^+$ 0-0 transition of CaF has been examined by the technique of intermodulated fluorescence spectroscopy ("Lamb dip"). The hyperfine structure due to ^{19}F and the spin-rotation fine structure of the X $^2\Sigma^+$ state was determined. Parameter values of $b = 104.0(9)$ MHz, $c = 58(6)$ MHz and $\gamma = 38.6(2)$ MHz were found for $v = 0$ of X $^2\Sigma^+$.

1. Introduction

The technique of intermodulated fluorescence spectroscopy has been described by several groups [1-3]. Considering the ease with which such spectra can now be obtained, the method has not been applied to molecular spectroscopy as often as one might expect. The availability of commercial tunable, single-mode dye lasers is changing this. We have examined the fine and hyperfine structure of the A $^2\Pi-X^2\Sigma^+$ transition of CaF.

2. Method

The CaF molecule was prepared in a Broida-type oven system [4] by the reaction of Ca metal and CF_3H . The CF_3H oxidant has an advantage over SF_6 or F_2 because it produces no chemiluminescence. Chemiluminescence results in additional noise by loading the photomultiplier with a large background signal. The total pressure (>99% Ar carrier gas) was about 0.5 Torr.

Output of a Coherent Radiation CR599-21 dye laser pumped by a Coherent Radiation CR-10 argon ion laser was split into two beams of roughly equal intensity. The total initial laser power was about 25

mW and power density in the fluorescence excitation region was approximately 10 mW/cm^2 in each beam. One beam was modulated at 20 Hz and the other at 450 Hz. The two beams were counter-propagated through the CaF "flame" and the fluorescence was detected through a 600 nm interference filter (Ditric, 10 nm bandpass) by a Hamamatsu R212 photomultiplier tube. Laser light was not focused in order to reduce power broadening. The laser beams crossed at an angle $< 1^\circ$ in order to prevent feedback into the dye laser. The intermodulated fluorescence signal was detected by using two phase sensitive detectors in series. Output from the first phase sensitive detector (450 Hz reference, $\tau \approx 5$ ms) was fed into the second (20 Hz reference, $\tau = 0.3$ s) to remove the Doppler background. We believe this to be simpler and more convenient than the usual single phase sensitive detector sum or difference frequency scheme.

Frequency calibration of observed splittings was accomplished with a homebuilt, Invar spaced, semi-confocal Fabry-Pérot of 300 MHz free spectral range. Absolute frequency calibration of each feature was made by simultaneously recording the outputs of the phase sensitive detectors, Fabry-Pérot transmissions, and the excitation spectrum of iodine. I_2 reference lines were identified using the atlas of Gerstenkorn and Luc [5]. The A $^2\Pi-X^2\Sigma^+$ 0-0 CaF spectrum was assigned by comparison with a calculated spectrum made using recently determined accurate constants [6].

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3. Results and discussion

The observed spin-rotation and hyperfine splittings are recorded in table 1. The observed pattern of lines is illustrated by fig. 1. This pattern is identical to that observed by Carrington et al. [7] in the $A^2\Pi-X^2\Sigma^+$ spectrum of $^{13}\text{CO}^+$. Their hamiltonian is used in our analysis, after conversion to Frosch and Foley [8] parameters.

The linewidth (fwhm) of most of our lines is about 40 MHz, due largely to power broadening. By decreasing the power we were able to reduce the linewidth to as narrow as 25 MHz but with an unacceptable reduction in the signal-to-noise ratio (due to laser amplitude fluctuations, not shot noise). The A-X lifetime of 20 ns [9] corresponds to a natural linewidth of 8 MHz. The accuracy of our data is about 6 MHz for hyperfine splittings and 23 MHz for spin-rotation splittings (based on rms deviations of our fit).

The data of table 1 contained no evidence of HFS in the $A^2\Pi$ state so the data were fit by considering only the ground $X^2\Sigma^+$ state. An upper limit of 10 MHz was established for the $[a + (b + c)/2]$ constant

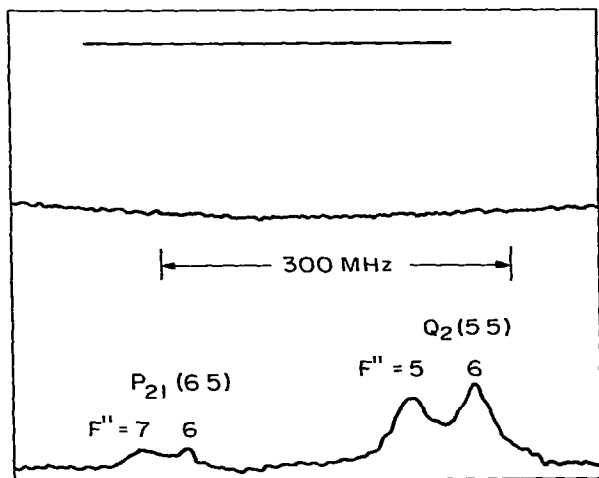


Fig. 1. Fine and hyperfine structure of a rotational line in the CaF $A^2\Pi_{3/2}-X^2\Sigma^+ 0-0$ band. The top trace is the excitation scan, limited in resolution by the Doppler effect, of this spectral region. (The baseline is at the top in this scan.) The lower trace shows the transitions from $N'' = 6$ to $J' = 5.5$. The weak satellite transition $P_{21}(6,5)$, separated by mainly the spin-rotation splitting of the $X^2\Sigma^+$ state from $Q_2(5,5)$, is clearly resolved.

Table 1

N''	Spin-rotation splitting ^{a)} (MHz)	Hyperfine structure splitting (MHz)	
		$P_{21}(N'')$	$Q_2(N'')$
5	201(-14) ^{b)}	35(-5) ^{b)}	56(-8) ^{b)}
6	234(-19)	38(-3)	55(-7)
47	1725(-109)	46(-4)	53(-1)
		$Q_{21}(N'')$	$R_2(N'')$
2	107(4)	26(-2)	72(-1)
3	140(0)	34(0)	72(2)
5	199(-16)	40(1)	65(1)
6	258(5)	42(1)	61(-1)
7	301(10)	44(1)	62(1)
8	338(8)	44(0)	61(0)
9	371(3)	45(0)	64(4)
10	410(3)	44(-1)	59(0)
11	454(9)	44(-2)	61(3)
12	489(5)	45(-1)	57(-1)
13	534(12)	46(0)	58(1)
14	558(-3)	45(-2)	59(2)
15	609(10)	48(1)	56(0)
16	645(7)	50(2)	57(1)
17	668(-8)	47(0)	55(-1)
		$P_1(N'')$	$Q_{12}(N'')$
3	142(2)	35(1)	82(12)
4	174(-3)	38(2)	64(-3)
6	251(-3)	42(1)	61(-2)
9	381(13)	45(1)	65(5)
12	488(4)	49(3)	63(5)
13	530(8)	45(-2)	60(2)
14	580(19)	45(-0)	57(1)
25	1013(28)	52(3)	60(5)
26	1036(13)	44(-5)	57(2)
27	1086(24)	48(-1)	55(0)
		$Q_1(N'')$	$R_{12}(N'')$
3	143(3)	36(3)	67(-3)
4	195(18)	40(4)	62(-4)
5	217(2)	33(-7)	61(-3)
6	251(-2)	35(-6)	49(-13)
7	292(1)	46(4)	51(-10)
8	338(8)	50(7)	55(-5)
9	377(8)	49(5)	55(-5)
12	482(-2)	46(0)	53(-4)
32	1254(-1)	56(6)	50(-4)
33	1338(46)	57(7)	51(-4)
34	1384(52)	57(7)	60(5)

^{a)} Defined by eq. (1).

^{b)} Brackets are (observed-calculated) in MHz.

of the A state. For each pattern of four lines, as shown in fig. 1, the energy level differences are given by

$$E_{N'', J'' = N'' + 1/2, F'' = N'' + 1} - E_{N'', N'' - 1/2, N'' - 1} \\ = [\gamma + c/(2N - 1)(2N + 3)](N + \frac{1}{2}), \quad (1)$$

$$E_{N'', N'' + 1/2, N'' + 1} - E_{N'', N'' + 1/2, N''} \\ = \frac{1}{2}\gamma(N + \frac{1}{2}) + \frac{1}{4}[2b + c/(2N + 3)] \\ - \frac{1}{4}[\gamma^2(2N + 1)^2 - 2\gamma(2b + c) + (2b + c)^2]^{1/2} \quad (2)$$

and

$$E_{N'', N'' - 1/2, N'' - 1} - E_{N'', N'' - 1/2, N''} \\ = -\frac{1}{4}\gamma(N + \frac{1}{2}) + \frac{1}{4}[2b - c/(2N - 1)] \\ + \frac{1}{4}[\gamma^2(2N + 1)^2 - 2\gamma(2b + c) + (2b + c)^2]^{1/2} . \quad (3)$$

These level separations were used in a simultaneous, nonlinear, least squares fit. The fits were made using the Troll computer language [10].

The results were $b = 104.0(9)$ MHz, $c = 58(6)$ MHz and $\gamma = 38.6(2)$ MHz for the $v = 0 X^2\Sigma^+$ state (uncertainties are one- σ values). The value of the b constant agrees very well with the value of 106 MHz obtained from ESR spectra of CaF trapped in a neon matrix [11]. The agreement for the c constant is not as good, the matrix value is 43 MHz. However the c parameter is more difficult to determine by intermodulated fluorescence than in the ESR experiment because rotational averaging washes out the effect of this anisotropic interaction. On the other hand, intermodulated fluorescence removes matrix interactions and allows excited states to be probed.

The value of γ has also been determined by microwave-optical double resonance to be 39(2) MHz [12]. The microwave-optical double resonance experiment could not resolve the hyperfine structure. This was due mainly to the $\Delta F = \Delta J$ selection rule and the small variation of HFS with N in the ground state. The microwave radiation probes only the small changes in HFS, while optical radiation, in an intermodulated fluorescence experiment, allows the complete splitting to be resolved.

The results are consistent with a simple ionic picture of the electronic structure of CaF. The $A^2\Pi - X^2\Sigma^+$ transition involves excitation of a nonbonding s-like electron centered on Ca^+ to a p-like orbital, also centered on Ca^+ . This explains the small spin density on F in the ground state and the even smaller hyper-

fine structure in the excited state. In the $A^2\Pi$ state the F atom lies in a nodal plane so the Fermi contact contribution to the HFS is zero. Furthermore the p-like orbital is centered on Ca^+ so the unpaired electron is too far away to give rise to a measurable effect at F^- .

Note added in proof. Recently Childs and Goodman [Phys Rev. Letters 44 (1980) 316] have observed spin-rotation and hyperfine structure of the $CaF X^2\Sigma^+$ state in the P_1 and Q_{12} branches of the $A^2\Pi - X^2\Sigma^+(0,0)$ band. They used an rf-optical double resonance technique on a CaF molecular beam to obtain constants in agreement with, but much more accurate than, our analysis. The variation of "effective" spin-rotation constant observed by them and us is due to a change from $b\beta_S$ to $b\beta_J$ coupling as N increases. This effect is entirely accounted for in the complete Frosch and Foley hamiltonian [8] from which our eqs. (1)-(3) are derived.

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