

THE MILLIMETER-WAVE SPECTRUM OF THE CaF RADICAL ($X^2\Sigma^+$)

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ABSTRACT

The pure rotational spectrum of the CaF radical has been measured in the laboratory using millimeter/sub-mm direct absorption spectroscopy. Fourteen rotational transitions have been detected originating in the $v = 0$ mode of the species. Rotational lines of the vibrationally excited $v = 1, 2$, and 3 states have also been observed. Spin-rotation splittings, as well as hyperfine interactions arising from the nuclear spin of the fluorine atom, were resolved in the CaF spectra. Rotational, fine-structure, and in some cases, hyperfine parameters were determined for the various vibrational modes of the molecule from a nonlinear least-squares fit to the data, using a $^2\Sigma$ Hamiltonian, and are in agreement with past measurements. The newly measured rest frequencies for CaF, which are accurate to at least ± 100 kHz, will enable astronomical searches to be conducted for the molecule in interstellar and circumstellar gas. Given the recent detection of AlF in IRC +10216, metal fluoride species may be more abundant than previously thought.

Subject headings: ISM: molecules — line: identification — molecular data

1. INTRODUCTION

One of the more interesting recent results for astrochemistry has been the detection of the metal-bearing chloride species AlCl, KCl, and NaCl, toward the circumstellar envelope of the late-type carbon star IRC +10216 (Cernicharo & Guélin 1987). Such identifications are surprising, given the cosmic abundances of the metal elements and chlorine, relative to hydrogen. For example, aluminum and sodium have abundances of $\sim 2 \times 10^{-6}$, and those of potassium and chlorine are almost a factor of 10 smaller than this value. Yet, these alkali and transition metal chlorides are present in circumstellar gas at readily detectable levels.

Another very unexpected result for interstellar chemistry has been the detection of a metal fluoride molecule, AlF, toward IRC +10216. Cernicharo & Guélin (1987) claimed a tentative identification of this species on the basis of three weak transitions observed at 2 and 3 mm in this object. Very recently, Ziurys, Apponi, & Phillips (1994) confirmed the identification of AlF by detecting three additional transitions at 1.2 and 0.8 mm toward the same source. The cosmic abundance of fluorine is about 5×10^{-8} , relative to hydrogen, and therefore the presence of any fluoride molecule in interstellar gas is unlikely, especially when coupled with a metal atom. The observation of six separate transitions of AlF, however, is solid evidence for the existence of this species in the IRC +10216 envelope.

The presence of aluminum fluoride in circumstellar gas suggests that other metal-bearing fluoride species might be present in the ISM, at least toward IRC +10216. Rest frequencies for these molecules are generally not available, especially for those that contain the more cosmically abundant metals. Thus, astronomical searches for these types of compounds have been limited in their scope.

One metal fluoride radical that might be present in interstellar and circumstellar gas is calcium fluoride, CaF. Although a calcium-bearing molecule has yet to be observed in the ISM,

species containing this element may be present, since calcium has a cosmic abundance similar to that of aluminum.

Calcium fluoride has been studied in the past by various spectroscopic techniques. These investigations include the measurement of several optical transitions (e.g., Field, Harris, & Tanaka 1975; Dulick, Bernath, & Field 1980; Bernath, Cummins, & Field 1980; Bernath & Field 1980), as well as MODR (Nakagawa et al. 1978) and laser-rf double resonance studies (Childs, Goodman, & Goodman 1981). Also some unpublished microwave work has been done by G. Weiler, whose rotational constants were referenced by Ernst, Kändler, & Knüppel (1992).

In this paper we present the first measurements of the pure rotational spectrum of CaF in its $v = 0, 1, 2$, and 3 vibrational states in the 100–400 GHz range. The spectra were obtained using millimeter/sub-mm direct absorption techniques, and have resulted in determining the rotational rest frequencies of the radical to an accuracy of better than ± 100 kHz. These data should now allow viable astronomical observations for the molecule to be carried out.

2. EXPERIMENTAL

The measurements were performed with the Arizona State University mm/sub-mm spectrometer that is described in detail elsewhere (Ziurys et al. 1993). The frequency sources for the spectrometer are phase-locked Gunn oscillators (J. E. Carlstrom Co.); for the shorter wavelength work, Schottky diode multipliers are used (Millitech Corp.). The gas cell is a double-pass, quasi-optically designed system 0.5 m in length. The detector is a helium-cooled InSb bolometer (Cochise Instruments). The spectrometer is computer-controlled through an IEEE bus. Phase sensitive detection is employed at 2f by FM modulation of the source and use of a lock-in amplifier.

CaF was synthesized by the reaction of calcium vapor and F_2 gas. The vapor was generated in a Broida-type oven and flowed into the cell with ~ 20 mtorr of argon carrier gas. Approximately 20 mtorr of fluorine gas was added to the hot calcium vapor to produce CaF radicals. The species could also

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be generated by first running the F_2 gas through a 2.4 GHz microwave discharge, but this technique was found to work no better than adding the fluorine gas directly. No chemiluminescence was observed on combining F_2 with the metal vapor.

The frequencies for the individual transitions were determined by fitting Gaussian curves to the line profiles. The curves were typically fit to data taken with scan widths of 3 MHz.

3. RESULTS

Fourteen separate rotational transitions were measured for the ground ($v = 0$) vibrational state of CaF, and are listed in Table 1. Calcium fluoride has a $^2\Sigma^+$ ground electronic state, and consequently its spectrum exhibits fine-structure splittings due to the interaction of the spin angular momentum S of the single unpaired electron and the molecule's rotational angular momentum N . The resulting fine structure is labeled by quantum number J , where $J = N + S$. In addition, the most abundant isotope of fluorine, ^{19}F , has a nuclear spin of $\frac{1}{2}$, which can result in hyperfine structure labeled by quantum number F , where $F = J + I$. As Table 1 illustrates, the hyperfine structure in the lower six transitions measured in this work was resolved, resulting in four components per transition. At higher frequencies, however, these interactions are sufficiently small such that the hyperfine structure is completely collapsed in the data. Hence, transitions $N = 10 \rightarrow 11$ and higher are only split by spin-rotation interactions, and thus consist of two spectral components.

The progression of the hyperfine structure for CaF is shown in Figure 1. In the figure, spectra of the $N = 6 \rightarrow 7$, $9 \rightarrow 10$, and $16 \rightarrow 17$ rotational transitions are displayed. For the $N = 6 \rightarrow 7$ transition near 143.7 GHz, four distinct hyperfine components are present. For the $N = 9 \rightarrow 10$ line at 205.3 GHz, however, the four components are barely resolved. Finally, at the $N = 16 \rightarrow 17$ transition, only two spectral features remain.

Tables 2, 3, and 4 list the rotational transitions observed for the $v = 1$, 2, and 3 excited vibrational modes, respectively. Four rotational transitions were measured for each excited mode, but all were obtained for the transitions $N = 14 \rightarrow 15$ and higher. Thus, no hyperfine splitting was observed in these data, but each transition consists of doublets resulting from spin-rotation interactions. These splittings were clearly resolved in each transition.

Table 5 lists the values of the spectroscopic constants determined for CaF in this work for the four vibrational modes observed. These constants were determined from a nonlinear least-squares fit to the data using a $^2\Sigma$ Hamiltonian. There were difficulties fitting the $v = 0$ data because the spin-rotation splitting changes significantly with N as the molecule shifts from a b_{ps} to a b_{pJ} coupling scheme (e.g., Bernath et al. 1980). Hence, the $v = 0$ data was fit in two separate sets: one group consisting of the six lower transitions where hyperfine structure was resolved, and another set formed from eight higher transitions where this structure was not observed. From the first data set, the hyperfine constants b and c (Frosch and Foley notation) were determined, although in the fit the nuclear spin-rotation constant c_I was held fixed to the value derived by Childs et al. (1981). For the second set, b , c , and c_I were set to zero in the fit. For both data sets, a better fit was obtained by fixing the centrifugal distortion correction to the spin-rotation constant, γ_D , to a small value (0.005 MHz). The rotational constants B_0 and D_0 determined from the two analyses were identical, as is expected. The derived value for the spin-rotation

TABLE 1
OBSERVED TRANSITION FREQUENCIES OF CaF: $X^2\Sigma^+ (v = 0)^a$

$N \rightarrow N'$	$J \rightarrow J'$	$F \rightarrow F'$	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
$3 \rightarrow 4$	$5/2 \rightarrow 7/2$	$2 \rightarrow 3$	82,117.481	0.022
		$3 \rightarrow 4$	82,120.422	-0.005
	$7/2 \rightarrow 9/2$	$3 \rightarrow 4$	82,153.003	0.011
		$4 \rightarrow 5$	82,156.265	0.002
$4 \rightarrow 5$	$7/2 \rightarrow 9/2$	$3 \rightarrow 4$	102,648.890	-0.001
		$4 \rightarrow 5$	102,651.013	-0.034
	$9/2 \rightarrow 11/2$	$4 \rightarrow 5$	102,685.674	0.009
		$5 \rightarrow 6$	102,687.966	-0.001
$6 \rightarrow 7$	$11/2 \rightarrow 13/2$	$5 \rightarrow 6$	143,706.597	-0.023
		$6 \rightarrow 7$	143,707.833	-0.031
	$13/2 \rightarrow 15/2$	$6 \rightarrow 7$	143,744.652	0.017
		$7 \rightarrow 8$	143,745.951	0.022
$7 \rightarrow 8$	$13/2 \rightarrow 15/2$	$6 \rightarrow 7$	164,232.133	-0.018
		$7 \rightarrow 8$	164,233.167	0.030
	$15/2 \rightarrow 17/2$	$7 \rightarrow 8$	164,270.482	-0.024
		$8 \rightarrow 9$	164,271.540	0.014
$8 \rightarrow 9$	$15/2 \rightarrow 17/2$	$7 \rightarrow 8$	184,754.965	-0.026
		$8 \rightarrow 9$	184,755.849	0.057
	$17/2 \rightarrow 19/2$	$8 \rightarrow 9$	184,793.557	-0.040
		$9 \rightarrow 10$	184,794.460	0.039
$9 \rightarrow 10$	$17/2 \rightarrow 19/2$	$8 \rightarrow 9$	205,274.793	-0.006
		$9 \rightarrow 10$	205,275.498	0.036
	$19/2 \rightarrow 21/2$	$9 \rightarrow 10$	205,313.554	-0.044
		$10 \rightarrow 11$	205,314.275	-0.003
$10 \rightarrow 11$	$19/2 \rightarrow 21/2$	$9 \rightarrow 10$	225,791.612	0.081
		$10 \rightarrow 11$		
	$21/2 \rightarrow 23/2$	$10 \rightarrow 11$	225,830.421	-0.071
		$11 \rightarrow 12$		
$11 \rightarrow 12$	$21/2 \rightarrow 23/2$	$10 \rightarrow 11$	246,304.320	0.048
		$11 \rightarrow 12$		
	$23/2 \rightarrow 25/2$	$11 \rightarrow 12$	246,343.253	-0.015
		$12 \rightarrow 13$		
$12 \rightarrow 13$	$23/2 \rightarrow 25/2$	$11 \rightarrow 12$	266,812.956	-0.008
		$12 \rightarrow 13$		
	$25/2 \rightarrow 27/2$	$12 \rightarrow 13$	266,851.997	-0.001
		$13 \rightarrow 14$		
$13 \rightarrow 14$	$25/2 \rightarrow 27/2$	$12 \rightarrow 13$	287,317.207	-0.062
		$13 \rightarrow 14$		
	$27/2 \rightarrow 29/2$	$13 \rightarrow 14$	287,356.382	0.039
		$14 \rightarrow 15$		
$14 \rightarrow 15$	$27/2 \rightarrow 29/2$	$13 \rightarrow 14$	307,816.804	-0.047
		$14 \rightarrow 15$		
	$29/2 \rightarrow 31/2$	$14 \rightarrow 15$	307,855.987	0.019
		$15 \rightarrow 16$		
$15 \rightarrow 16$	$29/2 \rightarrow 31/2$	$14 \rightarrow 15$	328,311.375	0.003
		$15 \rightarrow 16$		
	$31/2 \rightarrow 33/2$	$15 \rightarrow 16$	328,350.539	0.003
		$16 \rightarrow 17$		
$16 \rightarrow 17$	$31/2 \rightarrow 33/2$	$15 \rightarrow 16$	348,800.479	-0.015
		$16 \rightarrow 17$		
	$33/2 \rightarrow 35/2$	$16 \rightarrow 17$	348,839.720	0.012
		$17 \rightarrow 18$		
$17 \rightarrow 18$	$33/2 \rightarrow 35/2$	$16 \rightarrow 17$	369,283.882	0.001
		$17 \rightarrow 18$		
	$35/2 \rightarrow 37/2$	$17 \rightarrow 18$	369,323.163	0.015
		$18 \rightarrow 19$		

^a N , J , and F indicate the lower state; N' , J' , and F' refer to the upper state.

constant γ , however, was somewhat larger in the lower frequency data set as opposed to the higher frequency one (39.388 MHz vs. 38.780 MHz). Allowing γ_D to be a free parameter in the fit did not significantly change this result. As noted by Childs & Goodman (1980), however, the spin-rotation constant of CaF has been found to decrease by $\sim 15\%$ as N increases, becoming constant only at very large N (≥ 40). Since the data presented here concern relatively small N -values, a significant change in γ as N increases is expected.

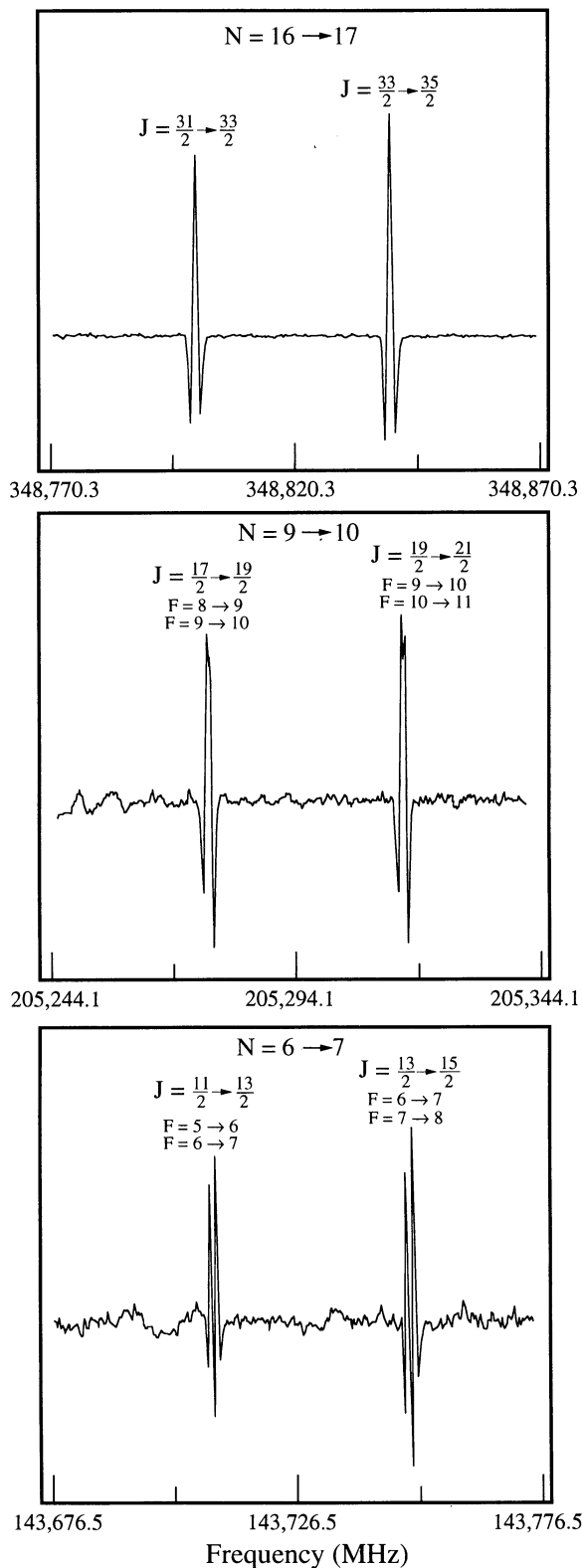


FIG. 1.—Spectra of the $N=6 \rightarrow 7$, $N=9 \rightarrow 10$, and $N=16 \rightarrow 17$ rotational transitions of CaF ($X^2\Sigma^+$) at 143.7, 205.3, and 348.8 GHz, respectively, observed in this work. Four hyperfine components are clearly present in the $N=6 \rightarrow 7$ spectrum, but are barely resolved in the $N=9 \rightarrow 10$ data. They have completely collapsed in the $N=16 \rightarrow 17$ spectrum. Each of these spectra is 100 MHz wide in frequency, and represents one single, 4 minute scan. The lines appear in emission because of the detection scheme employed.

TABLE 2
OBSERVED TRANSITION FREQUENCIES OF CaF : $X^2\Sigma^+$ ($v=1$)^a

$N \rightarrow N'$	$J \rightarrow J'$	$F \rightarrow F'$	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
14 → 15.....	27/2 → 29/2	13 → 14	305,627.465	-0.009
		14 → 15		
	29/2 → 31/2	14 → 15	305,666.292	0.010
15 → 16.....	29/2 → 31/2	14 → 15	325,976.002	-0.013
		15 → 16		
	31/2 → 33/2	15 → 16	326,014.872	0.003
16 → 17.....	31/2 → 33/2	15 → 16	346,319.161	0.006
		16 → 17		
	33/2 → 35/2	16 → 17	346,358.067	0.009
17 → 18.....	33/2 → 35/2	16 → 17	366,656.573	0.016
		17 → 18		
	35/2 → 37/2	17 → 18	366,695.490	-0.022

^a N , J , and F refer to the lower state; N' , J' , and F' indicate the upper state.

TABLE 3
OBSERVED TRANSITION FREQUENCIES OF CaF : $X^2\Sigma^+$ ($v=2$)^a

$N \rightarrow N'$	$J \rightarrow J'$	$F \rightarrow F'$	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
14 → 15.....	27/2 → 29/2	13 → 14	303,447.193	0.001
		14 → 15		
	29/2 → 31/2	14 → 15	303,485.690	0.002
15 → 16.....	29/2 → 31/2	14 → 15	323,650.353	-0.010
		15 → 16		
	31/2 → 33/2	15 → 16	323,688.911	0.005
16 → 17.....	31/2 → 33/2	15 → 16	343,848.125	-0.009
		16 → 17		
	33/2 → 35/2	16 → 17	343,886.737	0.011
17 → 18.....	33/2 → 35/2	16 → 17	364,040.182	0.018
		17 → 18		
	35/2 → 37/2	17 → 18	364,078.792	-0.018

^a N , J , and F refer to the lower state; N' , J' , and F' indicate the upper state.

TABLE 4
OBSERVED TRANSITION FREQUENCIES OF CaF : $X^2\Sigma^+$ ($v=3$)^a

$N \rightarrow N'$	$J \rightarrow J'$	$F \rightarrow F'$	ν_{obs} (MHz)	$\nu_{\text{obs}} - \nu_{\text{calc}}$ (MHz)
14 → 15.....	27/2 → 29/2	13 → 14	301,276.113	-0.012
		14 → 15		
	29/2 → 31/2	14 → 15	301,314.338	0.023
15 → 16.....	29/2 → 31/2	14 → 15	321,334.543	-0.007
		15 → 16		
	31/2 → 33/2	15 → 16	321,372.772	-0.015
16 → 17.....	31/2 → 33/2	15 → 16	341,387.589	0.016
		16 → 17		
	33/2 → 35/2	16 → 17	341,425.854	-0.005
17 → 18.....	33/2 → 35/2	16 → 17	361,434.859	0.002
		17 → 18		
	35/2 → 37/2	17 → 18	361,473.193	-0.003

^a N , J , and F refer to the lower state; N' , J' , and F' indicate the upper state.

TABLE 5
MOLECULAR CONSTANTS FOR CaF: $X^2\Sigma^+$ ^a

Species	Constant	This Work (MHz)	Previous Studies (MHz)
CaF	B_e	10,304.29 (11)	10,304.23 (63) ^b
	α_e	73.584 (96)	73.54 (45) ^b
	γ_e	0.151 (24)	...
CaF ($v = 0$)...	B_v	10,267.5387 (37)	10,267.5379 (90) ^c
	D_v	0.014060 (24)	0.014054 (90) ^c
	γ_v	39.388 (64) ^d	39.65892 (6) ^e
	γ_D	0.0005 ^f	...
	b	111.5 (2.6)	107.7687 (6) ^e
	c	33.3 (6.9)	41.175 (3) ^e
	c_I	0.0290 ^f	0.0290 (12) ^e
CaF ($v = 1$)...	B_v	10,194.5563 (24)	10,194.4 (2.7) ^g
	D_v	0.0140599 (43)	...
	γ_v	38.470 (21)	...
	γ_D	0.0005 ^f	...
CaF ($v = 2$)...	B_v	10,121.8765 (21)	10,121.5 (1.4) ^b
	D_v	0.0140630 (37)	...
	γ_v	38.159 (18)	...
	γ_D	0.0005 ^f	...
CaF ($v = 3$)...	B_v	10,049.5023 (24)	...
	D_v	0.0140625 (42)	...
	γ_v	37.853 (20)	...
	γ_D	0.0005 ^f	...

^a Errors in parentheses are 3 σ and apply to last quoted decimal places.

^b From Dulick et al. 1980.

^c From G. Weiler, unpublished Diplom thesis.

^d Spin-rotation constant derived from fitting only the data that showed hyperfine splittings i.e., lower N transitions (see text).

^e From Childs et al. 1981.

^f Held fixed (see text).

^g From Nakagawa et al. 1978.

Because there was no evidence of hyperfine structure in $v = 1, 2$, and 3 spectra for CaF, these data were fit neglecting hyperfine interactions. Hence, B_v , D_v , and γ_v were the only constants determined for these excited modes. As in the $v = 0$ case, the fit was obtained by fixing γ_D to a small constant value.

Also given in Table 5 are the parameters derived for CaF from other spectroscopic studies. The rotational constants for the $v = 0$ mode derived independently in this work are in good agreement with the unpublished microwave determinations. The fine and hyperfine constants also agree with those of

Childs et al. (1981) within the experimental errors. The constants derived for the $v = 1, 2$, and 3 states improve considerably on past values.

The errors quoted in Table 5 are purely statistical, based on the goodness of the fit to the data. There are other possible sources of error, such as frequency drift of the signal generator used as the phase-lock reference. The derived constants reproduce the data to $\nu_{\text{obs}} - \nu_{\text{calc}} \lesssim 80$ kHz. The difference is rather larger because of the fast variation of γ with N quantum number. The overall uncertainty in the transitions measured here is estimated to be ± 100 kHz.

4. DISCUSSION

The bonding in CaF is thought to be primarily ionic (e.g., Bernath et al. 1980), similar to CaOH. Thus, the unpaired electron resides in a σ -type orbital centered on the calcium atom in a Ca^+F^- type structure. This ionic bonding scheme is supported by the relatively small value of the hyperfine constant b , which includes the Fermi contact term. Thus, the electron density at the F nucleus, which has the nuclear spin, is not very large, which is expected if the lone electron is primarily located on the metal atom.

The spin-rotation constant γ of CaF was found to vary significantly with N , as mentioned. The value determined here was 39.388 (64) MHz for the lower N transitions, and 38.780 (42) MHz for the higher N lines. This large systematic dependence of γ on N was first discovered by Childs & Goodman (1980), and apparently is unique to CaF. These authors attribute this effect to competition between the spin-rotation and hyperfine interactions, which are comparable in magnitude at small N . This competition partly decouples the spin from the rotational angular momentum in the lower rotational levels.

Measurements of the pure rotational spectrum of CaF should now enable a definitive search for the species in the interstellar medium. If the chemistry of this species is similar to AlF, it is likely that the radical is present in IRC + 10216. The dipole moment of CaF is 3.07 D (Childs et al. 1984).

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