

# THE CF RADICAL: TERAHERTZ SPECTRUM AND DETECTABILITY IN SPACE

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## ABSTRACT

Pure rotational transitions of the CF radical in its  $X^2\Pi_{3/2,1/2}$  states have been observed with two terahertz spectrometers using backward wave oscillators as radiation sources. The radical was generated by a DC discharge in a gaseous mixture of  $\text{CF}_4$  and Ar. We have measured 48 rotational lines in the frequency range from 455 to 1072 GHz covering  $J$ -values as high as 12.5. The achieved frequency precision is about 50 kHz, which is comparable to that of conventional microwave spectroscopy. In addition to these pure rotational transitions, two direct transitions between the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  states near 1062 GHz ( $J = 20.5\text{--}21.5$ ) have been identified for the first time. Together with the zero-field rotational transition frequencies available in the literature, the present data were analyzed by a least-squares fitting procedure using an effective Hamiltonian for the  $^2\Pi$  states. The determined constants are complete and accurate enough to predict new line positions with low estimated uncertainties of less than  $\sim 170$  kHz in the sense of a  $3\sigma$  deviation. These predictions should assist future astronomical searches of CF in the millimeter- and submillimeter-wave region.

*Subject headings:* ISM: molecules — line: identification — methods: laboratory — molecular data — radio lines: ISM — submillimeter

## 1. INTRODUCTION

The detection of fluorine-bearing molecules in interstellar space and circumstellar shells still contains an element of surprise and remains to some extent an ongoing puzzle. With a solar system abundance of about  $3 \times 10^{-8}$  relative to hydrogen, the abundance of fluorine lies only a factor of 6 below that of chlorine (Anders & Grevesse 1989), and two fluorine-containing molecules—HF (Neufeld et al. 1997) and AlF (Cernicharo & Guélin 1987)—have been detected in space. Other fluorine-bearing species may be present and detectable as well, and in this paper we present new measurements of the high-frequency rotational spectrum of the radical CF to aid in interstellar and circumstellar searches.

In view of the elemental abundances of Cl and F and the dominance of hydrogen, it is not surprising that the two simple diatomic hydrogen halides HCl and HF have been detected in interstellar clouds. Hydrogen chloride, HCl, was observed in emission by its  $J = 1\text{--}0$  transition toward OMC-1 (Blake, Keene, & Phillips 1985; Schilke, Phillips, & Wang 1995) and in absorption against the dust continuum emission of the molecular cloud Sagittarius B2 (Zmuidzinas et al. 1995). The fractional abundance of hydrogen chloride relative to molecular hydrogen was determined to be a few times  $10^{-10}$  in OMC-1 and  $1.1 \times 10^{-9}$  in Sgr B2. Based on these abundances, chemical analysis indicates a significant depletion (50–250) of elemental chlorine onto the dust grains.

Rather recently, based on observations with the *Infrared Space Observatory*, the  $J = 2\text{--}1$  transition of hydrogen fluoride (HF) at 2.463 THz was detected in absorption toward

the same cloud in Sgr B2 (Neufeld et al. 1997) against which HCl had been recorded earlier. The fractional abundance of HF relative to  $\text{H}_2$  was determined to be  $3 \times 10^{-10}$ , indicating (as with chlorine) a significant depletion of fluorine onto dust grains if one assumes that HF is the dominant carrier of gas-phase fluorine. In addition, HF has been widely observed by means of its vibration-rotation spectra in the cool atmospheres of stars in their red-giant phase (e.g., Jorissen, Smith, & Lambert 1992).

The less expected part of the halogen story, however, lies not in HF and HCl but in another class of molecules, the metal halides NaCl, AlCl, KCl, and AlF, detected toward the chemically rich circumstellar envelope of the late-type carbon star IRC + 10216. The rotational spectra of these metal halides was first observed in emission by Cernicharo & Guélin (1987). Their tentative AlF detection has been confirmed by Ziurys, Apponi, & Phillips (1994), who also reported upper limits on CaF and MgF. In addition, the observations of Ziurys et al. (1994) indicate that the emission of AlF is confined to the inner part ( $5''\text{--}10''$ ) of the carbon-rich circumstellar shell. The detection is actually in reasonable agreement with models that assume high-temperature thermodynamic equilibrium (Tsuji 1973; Sharp & Huebner 1990) and solar abundances. Since the envelope of IRC + 10216 is carbon rich and since the fluorine abundance may well exceed its solar value (Ziurys et al. 1994), IRC + 10216 is a possible source of the radical CF as well, although, as discussed later in a simplified thermodynamic argument, this radical may not be abundant at LTE, as compared with HF. The excitation in the relatively warm inner part of the envelope should be sufficient to excite medium- $J$  rotational transitions such as those reported.

The abundance of fluorine-containing molecules other than HF in dense molecular clouds is not expected to be

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large, as judged from the solar abundance of elemental fluorine (Anders & Grevesse 1989) and from the estimated depletion value of about 50 (Neufeld et al. 1997). In fact, Lee, Bettens, & Herbst (1996) completely neglected the contribution of fluorine-containing species in their calculation of fractional abundances in dense molecular clouds. Still, HF has subsequently been detected, and below we present an ion-molecule pathway that leads from HF to the CF radical. This pathway produces an abundance of CF not significantly less than HF.

To shed more light on the CF problem in space, we have extended the measurements of its rotational spectrum into the 1 THz region and combined our data with previous data in order to determine molecular constants that can be used for the accurate predictions of lines not studied in the laboratory.

## 2. ROTATIONAL SPECTRUM OF CF

The pure rotational spectrum of CF arises from two stacks of energy levels pertaining to the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  states, split by about  $77.2\text{ cm}^{-1}$  by the electronic spin-orbit interaction (Brown et al. 1986). As is true of "normal" species, the  $^2\Pi_{1/2}$  state is the lower of the two. The observed rotational transitions are split first by the effect of  $\Lambda$ -doubling and second by magnetic hyperfine interactions between the nuclear spin angular momentum,  $I$ , and the electronic orbital angular momentum,  $L$ , and spin angular momentum,  $S$ . The  $\Lambda$ -doubling is larger in the  $^2\Pi_{1/2}$  state than in the  $^2\Pi_{3/2}$  state (Kawaguchi et al. 1981). The rotational states are characterized by the rotational quantum numbers  $J$  and  $F$ , where  $F$  refers to the total angular momentum, and by a parity quantum number.

The first study of the rotational spectrum of CF was carried out by Saito et al. (1983), who measured transitions through 300 GHz in frequency. The electric dipole moment was measured by Carrington & Howard (1970) and Saito et al. (1983) to be  $\mu = 0.65 \pm 0.005\text{ D}$ ; this value is much smaller than typical values derived for the metal halides. Higher frequency measurements on the pure rotational spectrum of CF have been performed using far-infrared (FIR) laser magnetic resonance (LMR) spectroscopy (Saykally et al. 1982; Brown et al. 1986; Liu, Liu, & Davies 1995) and FIR laser sideband spectroscopy (Van den Heuvel, Meerts, & Dymanus 1982). These measurements lack the experimental accuracy and frequency resolution obtained with microwave spectroscopy. For deep astronomical searches, it is desirable to know line positions very accurately and to know the underlying hyperfine pattern if it exists. In this paper, we report such data for the CF rotational spectrum up to frequencies exceeding 1 THz. We also report revised molecular constants from a least-squares fit of the newly measured data together with selected data available in the literature.

## 3. EXPERIMENTAL PROCEDURES

The terahertz spectrometers at NAIR (Morino et al. 1997) and at Cologne (Winnewisser 1995) have been used for the new measurements presented here. The spectrometers in both laboratories are essentially the same. In the NAIR spectrometer, the submillimeter-wave radiation is produced by water-cooled, Russian-made backward wave oscillator tubes (BWOs). A wire-grid polarizer serves as a beam splitter directing about one-half of the submillimeter-

wave power to a harmonic mixer-diode and one-half to an absorption cell. The diode (made and provided by KOSMA, I. Physikalisches Institut, University of Cologne, Germany) is mounted at the edge of a waveguide through which millimeter-wave (mmw) local oscillator power at about 100 GHz is supplied. A mmw phase-locked Gunn oscillator or a mmw-synthesizer (KVARZ Co.) is used as a local oscillator. The intermediate frequency produced by the mixer-diode is locked at 350 MHz using a phase-lock-loop. The power transmitted through the absorption cell is detected on a magnetically tuned liquid helium-cooled InSb hot electron bolometer. The BWO signal is frequency modulated at 10 kHz and recorded by a  $2f$ -phase sensitive detection using a lock-in amplifier.

The CF radical was generated by a DC discharge cell in a gaseous mixture of  $\text{CF}_4$  and Ar. The cell at NAIR, made of a Pyrex glass tube of 1 m length and 79 mm inner diameter, is equipped with two stainless steel cylindrical electrodes of 0.1 mm thickness. The electrodes are separated from each other by about 0.5 m. A cooling jacket around the absorption cell keeps it at room temperature during the discharge operation. The discharge product was continuously pumped through a liquid nitrogen-cooled trap by a mechanical booster pump ( $160\text{ m}^3\text{ hr}^{-1}$ ) followed by a rotary pump ( $32.4\text{ m}^3\text{ hr}^{-1}$ ). A discharge current of about 200 mA was applied to a mixture of  $\sim 30$  mtorr  $\text{CF}_4$  and 260 mtorr Ar. In similar experiments at Cologne, a current of about 300 mA was applied to a mixture of 10 mtorr  $\text{CF}_4$  and 40 mtorr Ar. At Cologne, the discharge zone extends about 1.5 m and the outside of the cell was cooled to a temperature of 120–150 K.

## 4. OBSERVED SPECTRA AND ANALYSIS

The pure rotational transitions of CF were measured in a frequency range from 455 to 816 GHz at NAIR and from 901 to 1072 GHz at Cologne. A portion of the observed spectrum of CF, the  $J = 9.5\text{--}8.5$  transition in the  $^2\Pi_{3/2}$  state at 815 GHz, is shown in Figure 1. The hyperfine structure is clearly resolved with line widths that are essentially limited by Doppler broadening. Although for the  $\Delta J = +1$  tran-

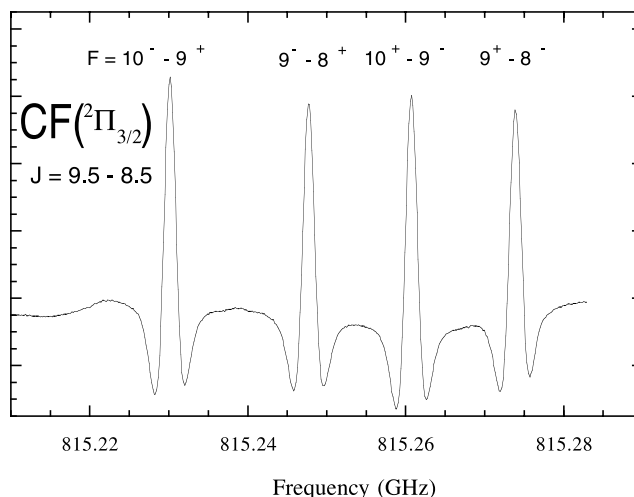


FIG. 1.—The observed  $J = 9.5\text{--}8.5$  transitions of CF in the  $^2\Pi_{3/2}$  state are reproduced. The line width is almost equal to the expected Doppler width (FWHM = 2.1 MHz). A bipolar square wave with 10 kHz was used for frequency modulation, and the spectral lines were recorded in the second derivative form.

TABLE 1  
OBSERVED AND CALCULATED FREQUENCIES OF THE ROTATIONAL TRANSITIONS OF CF IN THE  $X^2\Pi$  STATE

STATE	TRANSITION <sup>a</sup>		FREQUENCY (MHz)			<i>A</i> (s <sup>-1</sup> )	<i>E'</i> (cm <sup>-1</sup> )		
	<i>J'</i> ← <i>J''</i>	<i>F'</i> ← <i>F''</i>	Observed <sup>b</sup>	Calculated	<i>O</i> − <i>C</i>				
<sup>2</sup> Π <sub>1/2</sub> .....	1.5	0.5	1 +	1 −	123682.520(50) <sup>c</sup>	123682.534	−0.014	5.18E − 07	0.007
			2 −	1 +	124001.566(50) <sup>c</sup>	124001.639	−0.073	1.56E − 06	0.000
			1 −	0 +	124185.447(50) <sup>c</sup>	124185.453	−0.006	1.05E − 06	0.007
			1 −	1 +	124217.490(50) <sup>c</sup>	124217.494	−0.004	5.25E − 07	0.007
			2 +	1 −	124309.999(50) <sup>c</sup>	124310.000	−0.001	1.57E − 06	0.028
			1 +	0 −	124708.812(50) <sup>c</sup>	124708.842	−0.030	1.06E − 06	0.007
	2.5	1.5	2 −	2 +	...	206580.011	...	8.76E − 07	6.919
			3 +	2 −	206850.486(50) <sup>c</sup>	206850.579	−0.093	8.69E − 06	6.900
			2 +	1 −	206899.442(50) <sup>c</sup>	206899.431	0.011	7.82E − 06	6.909
			2 +	2 −	...	207115.286	...	8.83E − 07	6.909
			3 −	2 +	207127.411(50) <sup>c</sup>	207127.421	−0.010	8.73E − 06	6.937
			2 −	1 +	207207.496(50) <sup>c</sup>	207207.477	0.019	7.87E − 06	6.919
	3.5	2.5	3 +	3 −	...	289427.200	...	1.23E − 06	16.591
			4 −	3 +	...	289676.865	...	2.56E − 05	16.562
			3 −	2 +	289698.336(70) <sup>c</sup>	289698.226	0.110	2.44E − 05	16.572
			4 +	3 −	289941.435(50) <sup>c</sup>	289941.419	0.016	2.57E − 05	16.608
			3 −	3 +	...	289962.932	...	1.23E − 06	16.572
			3 +	2 −	289974.536(50) <sup>c</sup>	289974.611	−0.075	2.44E − 05	16.591
	4.5	3.5	4 −	4 +	...	372263.171	...	1.58E − 06	29.026
			5 +	4 −	...	372503.037	...	5.64E − 05	28.988
			4 +	3 −	...	372513.417	...	5.49E − 05	28.998
			5 −	4 +	...	372760.078	...	5.65E − 05	29.042
			4 −	3 +	...	372777.390	...	5.50E − 05	29.026
			4 +	4 −	...	372799.485	...	1.59E − 06	28.998
	5.5	4.5	5 +	5 −	455099.799(300) <sup>d</sup>	455099.356	0.443	1.94E − 06	44.223
			6 −	5 +	455335.115(50) <sup>d</sup>	455335.114	0.002	1.05E − 04	44.176
			5 −	4 +	455339.927(50) <sup>d</sup>	455339.905	0.021	1.04E − 04	44.186
			5 −	5 +	455636.522(150) <sup>d</sup>	455636.353	0.169	1.95E − 06	44.186
			6 +	5 −	455586.117(50) <sup>d</sup>	455586.139	−0.022	1.06E − 04	44.239
			5 +	4 −	455596.298(50) <sup>d</sup>	455596.263	0.035	1.04E − 04	44.223
	6.5	5.5	6 −	6 +	...	537940.356	...	2.30E − 06	62.183
			7 +	6 −	...	538175.333	...	1.77E − 04	62.128
			6 +	5 −	...	538176.874	...	1.74E − 04	62.138
			7 −	6 +	...	538420.788	...	1.77E − 04	62.199
			6 −	5 +	...	538427.139	...	1.75E − 04	62.183
			6 +	6 −	...	538478.113	...	2.30E − 06	62.138
	7.5	6.5	7 +	7 −	620788.351(300) <sup>d</sup>	620788.038	0.314	2.59E − 06	82.906
			7 −	6 +	621024.103(250) <sup>d</sup>	621023.823	0.279	2.72E − 04	82.853
			8 −	7 +	...	621024.336	−0.233	2.75E − 04	82.843
			8 +	7 −	621264.220(100) <sup>d</sup>	621264.278	−0.058	2.75E − 04	82.922
			7 +	6 −	621268.535(100) <sup>d</sup>	621268.470	0.065	2.72E − 04	82.906
			7 −	7 +	...	621326.604	...	2.60E − 06	82.853
	8.5	7.5	8 −	8 +	...	703642.705	...	2.92E − 06	106.393
			8 +	7 −	703879.797(100) <sup>d</sup>	703879.836	−0.039	4.00E − 04	106.332
			9 +	8 −	703881.767(100) <sup>d</sup>	703881.718	0.049	4.03E − 04	106.322
			9 −	8 +	704115.956(100) <sup>d</sup>	704116.051	−0.096	4.04E − 04	106.409
			8 −	7 +	704119.014(100) <sup>d</sup>	704118.945	0.069	4.01E − 04	106.393
			8 +	8 −	...	704182.104	...	2.93E − 06	106.332
	9.5	8.5	9 +	9 −	...	786503.534	...	3.27E − 06	132.643
			9 −	8 +	786743.289(100) <sup>d</sup>	786743.378	−0.089	5.63E − 04	132.575
			10 −	9 +	786746.304(100) <sup>d</sup>	786746.205	0.099	5.67E − 04	132.565
			10 +	9 −	786974.686(100) <sup>d</sup>	786974.788	−0.102	5.67E − 04	132.659
			9 +	8 −	786976.966(100) <sup>d</sup>	786976.880	0.086	5.64E − 04	132.643
			9 −	9 +	787044.035(200) <sup>d</sup>	787043.764	0.271	3.28E − 06	132.575
	10.5	9.5	10 −	10 +	...	869368.764	...	3.69E − 06	161.658
			10 +	9 −	869612.7(8) <sup>e</sup>	869612.241	0.5	7.66E − 04	161.582
			11 +	10 −	869616.7(8) <sup>e</sup>	869615.732	1	7.69E − 04	161.572
			11 −	10 +	869840.0(1.1) <sup>e</sup>	869838.425	1.6	7.70E − 04	161.674
			10 −	9 +	869840.0(1.1) <sup>e</sup>	869840.019	0	7.66E − 04	161.658
			10 +	10 −	...	869909.800	...	3.70E − 06	161.582
	11.5	10.5	11 +	11 −	...	952235.818	...	4.06E − 06	193.437
			11 −	10 +	952483.408(100) <sup>f</sup>	952483.545	−0.138	1.01E − 03	193.353

TABLE 1—Continued

STATE	TRANSITION <sup>a</sup>		FREQUENCY (MHz)			<i>A</i> (s <sup>−1</sup> )	<i>E'</i> (cm <sup>−1</sup> )	
	<i>J'</i> ← <i>J''</i>	<i>F'</i> ← <i>F''</i>	Observed <sup>b</sup>	Calculated	<i>O</i> − <i>C</i>			
<sup>2</sup> Π <sub>3/2</sub> .....	12.5	11.5	12− 11+	952487.553(100) <sup>f</sup>	952487.505	0.048	1.02E−03	193.344
			12+ 11−	952704.762(670) <sup>f</sup>	952704.191	0.571	1.02E−03	193.453
			11+ 10−	952704.762(670) <sup>f</sup>	952705.479	−0.717	1.01E−03	193.437
			11− 11+	...	952777.613	...	4.07E−06	193.353
			12− 12+	...	1035101.390	...	4.36E−06	227.980
			12+ 11−	1035353.542(350) <sup>f</sup>	1035353.770	−0.227	1.30E−03	227.889
			13+ 12−	1035358.121(350) <sup>f</sup>	1035358.056	0.065	1.31E−03	227.879
			13− 12+	1035569.392(580) <sup>f</sup>	1035568.652	0.740	1.31E−03	227.996
			12− 11+	1035569.392(580) <sup>f</sup>	1035569.759	−0.367	1.31E−03	227.980
			12+ 12−	...	1035643.878	...	4.37E−06	227.889
	2.5	1.5	2+ 2−	...	214548.854	...	6.51E−07	81.716
			2− 2+	...	214549.316	...	6.51E−07	81.716
			3+ 2−	214874.390(50) <sup>c</sup>	214874.340	0.050	6.51E−06	81.726
			3− 2+	214877.063(50) <sup>c</sup>	214877.108	−0.045	6.51E−06	81.727
			2+ 1−	215071.199(50) <sup>c</sup>	215071.067	0.132	5.87E−06	81.716
			2− 1+	215072.392(50) <sup>c</sup>	215072.433	−0.041	5.87E−06	81.716
			3− 3+	...	300600.849	...	1.15E−06	91.753
			3+ 3−	...	300601.758	...	1.15E−06	91.754
			4− 3+	300831.489(87) <sup>c</sup>	300831.399	0.090	2.39E−05	91.761
			4+ 3−	300836.491(70) <sup>c</sup>	300836.540	−0.049	2.39E−05	91.761
	3.5	2.5	3− 2+	300926.272(87) <sup>c</sup>	300926.336	−0.064	2.28E−05	91.753
			3+ 2−	300929.490(70) <sup>c</sup>	300929.549	−0.059	2.28E−05	91.754
			4+ 4−	...	386561.095	...	1.61E−06	104.655
			4− 4+	...	386562.570	...	1.61E−06	104.656
			5+ 4−	...	386733.502	...	5.69E−05	104.661
			5− 4+	...	386741.644	...	5.69E−05	104.662
			4+ 3−	...	386791.644	...	5.53E−05	104.655
			4− 3+	...	386797.352	...	5.53E−05	104.656
			5− 5+	...	472446.544	...	2.03E−06	120.420
			5+ 5−	...	472448.684	...	2.03E−06	120.421
	4.5	3.5	6− 5+	472578.497(70) <sup>d</sup>	472578.426	0.071	1.10E−04	120.425
			6+ 5−	472590.195(70) <sup>d</sup>	472590.145	0.050	1.10E−04	120.426
			5− 4+	472618.858(70) <sup>d</sup>	472618.951	−0.093	1.08E−04	120.420
			5+ 4−	472627.678(70) <sup>d</sup>	472627.758	−0.080	1.08E−04	120.421
			6+ 6−	...	558257.632	...	2.44E−06	139.046
			6− 6+	...	558260.509	...	2.44E−06	139.047
			7+ 6−	...	558358.825	...	1.88E−04	139.049
			7− 6+	...	558374.639	...	1.88E−04	139.051
			6+ 5−	...	558389.514	...	1.86E−04	139.046
			6− 5+	...	558401.971	...	1.86E−04	139.047
	5.5	4.5	7− 7+	...	643989.763	...	2.80E−06	160.531
			7+ 7−	...	643993.424	...	2.80E−06	160.532
			8− 7+	644066.396(50) <sup>d</sup>	644066.336	0.060	2.96E−04	160.533
			8+ 7−	644086.775(100) <sup>d</sup>	644086.700	0.076	2.96E−04	160.535
			7− 6+	644090.832(100) <sup>d</sup>	644090.956	−0.124	2.93E−04	160.531
			7+ 6−	644107.496(50) <sup>d</sup>	644107.554	−0.058	2.93E−04	160.532
			8+ 8−	...	729636.705	...	3.26E−06	184.871
			8− 8+	...	729641.168	...	3.26E−06	184.874
			9+ 8−	729692.752(50) <sup>d</sup>	729692.684	0.068	4.37E−04	184.873
			8+ 7−	729713.135(100) <sup>d</sup>	729713.278	−0.143	4.34E−04	184.871
	6.5	5.5	9− 8+	729718.082(100) <sup>d</sup>	729717.983	0.099	4.37E−04	184.876
			8− 7+	729734.413(50) <sup>d</sup>	729734.444	−0.031	4.34E−04	184.874
			9− 9+	...	815191.840	...	3.65E−06	212.065
			9+ 9−	...	815197.101	...	3.65E−06	212.068
			10− 9+	815230.129(50) <sup>d</sup>	815230.048	0.081	6.17E−04	212.066
			9− 8+	815247.696(50) <sup>d</sup>	815247.819	−0.123	6.14E−04	212.065
			10+ 9−	815260.707(50) <sup>d</sup>	815260.605	0.102	6.17E−04	212.070
			9+ 8−	815273.873(50) <sup>d</sup>	815273.916	−0.043	6.14E−04	212.068
			10+ 10−	...	900648.693	...	3.94E−06	242.109
			10− 10+	...	900654.722	...	3.94E−06	242.113
	7.5	6.5	11+ 10−	900671.231(100) <sup>f</sup>	900671.204	0.027	8.40E−04	242.109
			10+ 9−	900686.741(100) <sup>f</sup>	900686.901	−0.160	8.36E−04	242.109
			11− 10+	900707.276(200) <sup>f</sup>	900707.274	0.002	8.40E−04	242.115

TABLE 1—Continued

STATE	TRANSITION <sup>a</sup>		FREQUENCY (MHz)			<i>A</i> (s <sup>-1</sup> )	<i>E'</i> (cm <sup>-1</sup> )
	<i>J'</i> ← <i>J''</i>	<i>F'</i> ← <i>F''</i>	Observed <sup>b</sup>	Calculated	<i>O</i> − <i>C</i>		
<sup>2</sup> Π <sub>3/2</sub> ← <sup>2</sup> Π <sub>1/2</sub> .....	11.5	10.5	10− 9+	900718.190(200) <sup>f</sup>	−0.036	8.36E−04	242.113
			11− 11+	...	...	4.30E−06	274.999
			11+ 11−	...	...	4.30E−06	275.004
			12− 11+	...	...	1.11E−03	274.999
			11− 10+	...	...	1.11E−03	274.999
			12+ 11−	...	...	1.11E−03	275.006
	12.5	11.5	11+ 10−	...	...	1.11E−03	275.004
			12+ 12−	...	...	4.84E−06	310.732
			12− 12+	...	...	4.84E−06	310.739
			13+ 12−	1071239.264(100) <sup>f</sup>	0.158	1.43E−03	310.732
			12+ 11−	1071251.878(100) <sup>f</sup>	−0.093	1.43E−03	310.732
			13− 12+	1071286.701(100) <sup>f</sup>	−0.029	1.43E−03	310.740
	20.5	21.5	12− 11+	1071294.9(8) <sup>e</sup>	0.5	1.43E−03	310.739
			20+ 21−	1062430.504(100) <sup>f</sup>	0.102	...	698.454
			21+ 22−	1062593.474(100) <sup>f</sup>	−0.102	...	698.452

NOTE.—To convert energies to absolute values, it is necessary to add 4.1 cm<sup>-1</sup>.

<sup>a</sup> The sign of the *F* quantum number denotes the parity of states with the definition by Brown et al. 1978.

<sup>b</sup> The numbers in parentheses are estimated experimental uncertainties in units of the last quoted digits; see text for detail.

<sup>c</sup> Measured by microwave spectroscopy (Saito et al. 1983).

<sup>d</sup> Measured at NAIR.

<sup>e</sup> Measured by FIR laser sideband spectroscopy (Van den Heuvel, Meerts, & Dymanus 1982).

<sup>f</sup> Measured at Cologne.

sitions the intensities of the  $\Delta F = 0$  transitions are weaker than those of the  $\Delta F = +1$  transitions by 1–2 orders of magnitude, some  $\Delta F = 0$  transitions in the  $^2\Pi_{1/2}$  state were detected, albeit but barely, despite the very low intensities of the transitions. The  $\Delta F = 0$  transitions in the  $^2\Pi_{3/2}$  state, however, were not observed due to the unfavorable Boltzmann factor for that state.

The measured frequencies have been analyzed by a least-squares fitting procedure. The rotational frequencies measured by microwave (Saito et al. 1983) and laser sideband spectroscopy (Van den Heuvel, Meerts, & Dymanus 1982) were included in the present fit, while the LMR data were excluded. The experimental uncertainties were assumed to be 50 kHz for the microwave lines and 800 kHz for FIR laser sideband lines following the previous FIR-LMR analysis (Brown et al. 1986). Typical uncertainties for the present measurements are 50–100 kHz. Weights according to the quoted uncertainties were used in the least-squares analysis. When the absorption lines are very close to each other or are partly overlapping, larger uncertainties had to be assumed, i.e., 100–200 kHz. For fully overlapped lines or cases where the lines could only be observed with poor signal-to-noise ratio, much larger uncertainties were assumed.

An effective Hamiltonian in the Hund's case (a) basis set, expressed in the  $N^2$ -formalism (Brown et al. 1979), has been used for our analysis by adding magnetic hyperfine interaction terms (Brown et al. 1978) caused by  $^{19}\text{F}$ . The *e* and *f* labeling of these authors corresponds to the  $\pm$  parity labeling used here; the levels with parity  $+(-1)^{J-1/2}$  are of *e*, and levels with parity  $-(-1)^{J-1/2}$  are of *f* symmetry (Kopp & Hougen 1967; Brown et al. 1975). The measured transition frequencies used in the present analysis are listed in Table 1 along with uncertainties, quantum assignments, calculated frequencies, residuals (*O* − *C*: observed − calculated frequencies), Einstein *A* coefficients, and upper state energies. Predicted frequencies are also supplied for those tran-

sitions within the frequency range of interest but not measured.

With the help of predicted frequencies, calculated by using the molecular constants derived from a preliminary analysis of the pure rotational spectrum, we carried out a search for the  $^2\Pi_{3/2}$ – $^2\Pi_{1/2}$  transitions in the 1062 GHz region. Two absorption lines were located, the line frequencies of which are about 6 MHz higher than the predicted ones. These transitions, assigned as the  $^2\Pi_{3/2}$ ,  $J = 20.5$ ,  $F = 21^+$ ,  $20^+ \leftarrow ^2\Pi_{1/2}$ ,  $J = 21.5$ ,  $F = 22^-$ ,  $21^-$  lines, were included in the final fit and are listed in Table 1.

## 5. DISCUSSION

Altogether, 75 transitions including 21 lines from microwave spectroscopy and four lines from FIR laser sideband spectroscopy were included in the final fit. The determined molecular constants are listed in Table 2. The (weighted) standard deviation of the fit is 57.5 kHz.

The molecular constants obtained in the present study agree well with the previous constants determined by FIR-LMR data (Brown et al. 1986), as can be seen in Table 2. The spin-orbit interaction parameter,  $A_{\text{SO}}$ , was determinable because of the lines in the data set connecting the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  states with each other. However, because only two of these lines have been measured,  $A_{\text{SO}}$  is still not determined more accurately than the value quoted by Brown et al. (1986). Their FIR-LMR data contain more  $^2\Pi_{3/2}$ – $^2\Pi_{1/2}$  transitions.

The higher order, but very small and rather insignificant centrifugal distortion constant *H* was kept fixed to the value used in the analysis of the FIR-LMR data. We have adjusted the higher order  $\Lambda$ -type doubling parameters,  $p_D$  and  $q_D$ , to improve the fit although the obtained values are only slightly larger than their 1  $\sigma$  uncertainties. By employing the relation  $p_D + 2q_D = -2D(p + 2q)/B$  (Veseth 1970),  $q_D$  can

TABLE 2  
MOLECULAR CONSTANTS OF CF IN THE  $X^2\Pi$  STATE

Parameter	This Work	Brown et al.
$B$ .....	42197.0597(18) <sup>a</sup>	42197.0591(48)
$D$ .....	0.198885(11)	0.198748(44)
$H \times 10^9$ .....	-0.73 <sup>b</sup>	-0.73
$A$ .....	2314161.7(55)	2314157.64(45)
$\gamma$ .....	147.75(14)	147.69(17)
$\gamma_D \times 10^2$ .....	0.456(66)	-0.44(23)
$p$ .....	255.860(38)	255.983(88)
$p_D \times 10^2$ .....	-0.106(42)	-0.59
$q$ .....	0.750(12)	0.724(36)
$q_D \times 10^4$ .....	1.10(62)	-0.136
$a$ .....	705.90(10)	705.94(14)
$b_F$ .....	152.24(19)	151.19(49)
$c$ .....	-353.39(33)	-351.6(14)
$d$ .....	792.160(75)	792.195(98)
$C_I$ .....	0.052(13)	...

<sup>a</sup> The numbers in parentheses denote 1 standard deviation in the last quoted digits.

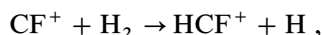
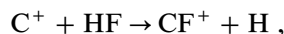
<sup>b</sup> Constrained at the value used by Brown et al. 1986.

also be estimated to be  $-1.53 \times 10^{-4}$  MHz by use of the values of  $B$ ,  $D$ ,  $p$ ,  $q$ , and  $p_D$  determined in the present study. The sign of  $q_D$  derived from this relation agrees with that assumed by Brown et al. (1986) but does not agree with the value obtained here. The  $q_D$  should be thus considered as a parameter required only for obtaining a good fit. The fit also revealed a value for the nuclear spin-rotation constant  $C_I(F)$  of the fluorine nucleus. The obtained value is in good agreement with that predicted from the other parameters via the relation  $|C_I/\gamma| = |a/A|$  (Endo, Saito, & Hirota 1983).

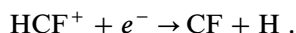
With a  $3\sigma$  uncertainty of 172 kHz, the precision of the predicted frequencies based on the molecular constants of the present study could be improved. Still, these frequency predictions, listed in Table 1, are highly accurate. Based on either the measured or predicted transition frequencies, a deep search for the CF radical should be conducted.

## 6. ASTROPHYSICAL IMPLICATIONS

In cold interstellar clouds, the CF radical can probably be formed from precursor HF by a sequence of exothermic ion-molecule reactions leading to the protonated ion  $\text{HCF}^+$ ,



followed by the dissociative recombination reaction

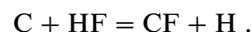


Thermodynamic information for all species other than  $\text{HCF}^+$  was taken from standard sources; the heat of formation for  $\text{HCF}^+$  was estimated from the work of Goto et al. (1994).

If the CF radical is then depleted mainly by reactions with ions rather than neutrals, it can achieve an abundance within an order of magnitude of that of the precursor HF. Although the CF radical is destroyed by ions such as  $\text{H}_3^+$ , which can be more abundant than  $\text{C}^+$ , the dipole moment

of HF is higher than that of CF so that ion-molecule reactions involving HF have larger rate coefficients at low temperatures. A deep search for CF toward the far-infrared continuum source Sgr B2, where HF has been detected (Neufeld et al. 1997), might be in order.

Although C and F are abundant in the inner envelopes of carbon-rich stars and HF has been detected toward a variety of cool stars (Jorissen et al. 1992), it is not obvious that CF can be found in these regions in sufficient abundance for detection. The basic problem is that, unlike AlF, which has been detected in the inner part of the IRC +10216 envelope, CF is not thermodynamically preferred so that if LTE prevails, its abundance will be relatively small. Consider the following equilibrium between CF and HF, which is important if C and HF are abundant:



The left-to-right reaction is endothermic, so the CF + H "products" can only be competitive at high temperatures. (Note that the corresponding reaction between Al and HF is quite exothermic.) We have checked the equilibrium coefficient  $K$ , where

$$K = n(\text{CF})n(\text{H})/n(\text{C})n(\text{HF}),$$

and the  $n(I)$  stand for assorted densities, for these processes through 2000 K in temperature (Chase et al. 1985) and find that even at this high temperature,  $K$  is less than unity so that the C and HF species are still favored. In particular, with the calculated value of  $K = 0.2$  at 2000 K and the assumption that the atomic carbon abundance is  $4 \times 10^{-4}$  times that of H, we obtain the CF abundance to be  $8 \times 10^{-5}$  that of HF. Of course, to be more definitive concerning the CF abundance, a complete thermodynamic analysis should be performed (see, e.g., Tsuji 1973), and many unanswered questions remain. A search for CF directed at the inner portion of IRC +10216 is thus still warranted.

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