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The Millimeter and Submillimeter Spectrum of CF_2 and Its Production in a dc Glow Discharge

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Extensive measurements of the free radical CF_2 were made with microwave techniques in the millimeter and submillimeter spectral region. For this work, CF_2 was observed in a glow discharge of fluorocarbons. Cell conditioning is shown to dramatically alter the concentration of CF_2. The rotational transition frequencies were analyzed in the context of Watson's reduced centrifugal distortion Hamiltonian. The results of this analysis include both precise rotation and distortion parameters and an accurate spectral map.

I. INTRODUCTION

CF_2 is one of the more stable gas-phase free radicals that has been detected in the laboratory. It is of substantial chemical interest as an initiator or intermediate in fluorocarbon reactions (*1*), and it is an important minor species in the upper atmosphere where it is created by the photodissociation of chlorofluoromethanes (*2*). In addition, many techniques for producing transient species for spectroscopic experiments involve chemical reactions with the discharge products of fluorocarbon compounds. CF_2 is a relatively abundant transient species in these discharges.

CF_2 has been the subject of a number of studies in the uv (*3–6*), the ir (*7*, *8*), and the microwave region (*9*, *10*). These studies have both elucidated the spectroscopic structure of the molecule and investigated its reaction dynamics. More recently, high-resolution ir diode laser spectroscopy has been used to study the rotational structure of the infrared spectrum (*11*). In that study, the previously available microwave data were used to define the rotational structure of the ground vibrational state. In this paper we report an extensive investigation of the ground vibrational state rotational structure that is based upon millimeter and submillimeter wave measurements. We also report several interesting features that dramatically alter the CF_2 content of the dc glow discharge that we use as a source.

II. EXPERIMENTAL DETAILS

We have previously discussed the techniques that we have developed for millimeter and submillimeter wave spectroscopy (*12*, *13*). In this experiment CF_2 was generated in a low-pressure glow discharge of simple fluorocarbons and observed *in situ*. The absorption cell was constructed from 4″-diam. Pyrex pipe and was approximately 60″ in length. Two hollow copper electrodes were placed in the pipe approximately 45″ apart. This cell is similar to that developed by Woods for the study of ions (*14*) and to those that we have used for the study of vibrational

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TABLE I

Transitions Used in the Analysis (MHz)

N(KP,KO)-N'(KP',KO')	Observed[a]	Obs.-Cal.	N(KP,KO)-N'(KP',KO')	Observed[a]	Obs.-Cal.
1(1 0)- 1(0 1)	77419.800	-0.192	15(3 12)-14(4 11)	-178003.160	-0.049
2(1 1)- 2(0 2)	79019.800	0.096	15(3 13)-14(4 10)	-182275.010	-0.064
2(0 2)- 1(1 1)	-28989.600	-0.039	16(1 15)-16(0 16)	225205.190	0.036
3(1 2)- 3(0 3)	81464.600	0.095	16(2 14)-15(3 13)	37171.550	-0.023
3(1 3)- 2(0 2)	142235.310	-0.038	16(2 15)-15(3 12)	-29651.620	0.060
4(1 3)- 4(0 4)	84808.300	0.196	17(2 15)-17(1 16)	199109.940	-0.031
4(0 4)- 3(1 3)	21500.100	-0.062	17(3 15)-16(4 12)	-135125.710	0.033
4(1 4)- 3(0 3)	162573.280	0.029	18(2 16)-18(1 17)	204474.230	-0.022
5(1 4)- 5(0 5)	89120.850	0.043	18(1 18)-17(2 15)	-27883.900	0.285
5(0 5)- 4(1 4)	47650.500	-0.020	20(1 19)-20(0 20)	316898.280	0.088
5(2 3)- 5(1 4)	219003.890	0.059	20(3 17)-19(4 16)	-43639.200	0.003
6(1 5)- 6(0 6)	94487.750	0.020	20(2 18)-19(3 17)	174766.500	0.026
6(1 6)- 5(0 5)	201220.660	-0.079	20(2 19)-19(3 16)	30220.600	-0.111
7(1 6)- 7(0 7)	101005.850	0.063	21(1 20)-21(0 21)	341850.170	0.027
7(0 7)- 6(1 6)	101286.860	-0.006	21(2 19)-21(1 20)	231110.360	0.032
7(1 6)- 6(2 5)	-44286.600	0.154	21(1 21)-20(2 18)	-59935.200	0.032
8(2 7)- 7(3 4)	-196683.610	0.034	21(2 20)-20(3 17)	40949.200	-0.028
9(2 7)- 9(1 8)	203153.060	-0.053	21(3 19)-20(4 16)	-43257.570	0.065
9(1 9)- 8(2 6)	-60493.616	0.016	21(4 17)-20(5 16)	-188947.830	-0.015
10(1 9)- 9(2 8)	45822.800	-0.018	21(4 18)-20(5 15)	-190912.640	0.014
10(1 10)- 9(2 7)	-48186.200	0.186	22(3 20)-21(4 17)	-21240.620	-0.033
11(2 9)-11(1 10)	196427.800	0.021	23(1 22)-23(0 23)	392868.920	0.047
11(1 11)-10(2 8)	-37747.200	-0.049	23(3 20)-22(4 19)	47701.900	0.081
12(2 10)-12(1 11)	194057.960	-0.021	23(4 19)-22(5 18)	-138332.670	0.019
12(1 12)-11(2 9)	-29340.600	0.063	24(2 23)-23(3 20)	60113.905	0.132
13(1 13)-12(2 10)	-23114.620	-0.073	24(3 22)-23(4 19)	20930.700	0.087
14(1 13)-14(0 14)	186690.320	-0.072	25(1 24)-25(0 25)	444307.130	-0.082
14(1 14)-13(2 11)	-19191.450	0.164	25(3 23)-24(4 20)	40826.150	0.082
14(2 12)-13(3 11)	-25894.000	-0.103	26(3 24)-25(4 21)	59733.478	-0.013
14(3 11)-13(4 10)	-203101.510	0.066	26(5 21)-25(6 20)	-223860.810	0.005
15(2 13)-15(1 14)	193105.360	0.026	26(5 22)-25(6 19)	-224435.320	-0.005
15(1 14)-14(2 13)	206435.730	0.022	27(3 24)-26(4 23)	185988.370	-0.065
15(2 14)-14(3 11)	-47950.800	-0.110	27(4 23)-26(5 22)	-31669.800	0.005

excitation and chemistry in laser plasmas (*15*) and for the spectroscopy of a number of unstable species (*16–18*). Neither the pressure, nor the discharge current were critical for the production of CF_2; typically, they were 40 μ and 50 mA, respectively. CF_4 and C_2F_6 were both used for the production of CF_2. Although the stability of the dc discharge was improved by increasing the series ballasting resistors, both gases produced discharges that were exceptionally noisy. The instability of fluorocarbon discharges is presumably due to the presence of atomic fluorine and fluorine-containing compounds. As we have noted previously (*19*), the dominant

TABLE I—*Continued*

N(KP,KO)-N'(KP',KO')	Observed[a]	Obs.-Cal.	N(KP,KO)-N'(KP',KO')	Observed[a]	Obs.-Cal.
27(4 24)-26(5 21)	-45212.600	-0.062	33(1 33)-32(2 30)	-346577.450	-0.005
27(5 22)-26(6 21)	-199112.370	0.026	34(5 29)-33(6 28)	-18635.900	-0.366
27(5 23)-26(6 20)	-199943.020	0.024	34(5 30)-33(6 27)	-26290.250	-0.155
28(2 27)-27(3 24)	50664.596	-0.196	34(7 27)-33(8 26)	-340834.490	-0.021
28(3 25)-27(4 24)	223518.260	-0.084	34(7 28)-33(8 25)	-340853.880	0.038
28(4 25)-27(5 22)	-21179.350	0.052	35(4 31)-35(3 32)	393051.710	-0.023
28(5 23)-27(6 22)	-174174.880	-0.085	35(1 34)-34(4 31)	-404514.910	0.035
28(5 24)-27(6 21)	-175358.630	-0.026	36(5 32)-35(6 29)	23589.370	-0.037
28(6 22)-27(7 21)	-331231.570	-0.038	38(4 34)-37(5 33)	339986.270	0.128
28(6 230-27(7 20)	-331279.550	-0.017	39(6 34)-38(7 31)	-59466.570	-0.070
29(4 25)-28(5 24)	25719.860	0.053	40(6 35)-39(7 32)	-34165.700	0.046
30(2 28)-30(1 29)	407321.840	-0.011	40(8 32)-39(9 31)	-350297.310	0.032
30(1 30)-29(2 27)	-259941.420	0.033	40(8 33)-39(9 30)	-350304.930	-0.057
30(4 27)-29(5 24)	26194.730	-0.013	41(4 37)-41(3 38)	397149.630	0.007
32(1 32)-31(2 29)	-317293.770	-0.027	43(5 38)-42(6 37)	256805.150	-0.068
32(3 30)-31(4 27)	142706.670	-0.001	47(9 38)-46(10 37)	-335422.800	-0.058
32(6 27)-31(7 24)	-233801.590	0.157	48(9 39)-47(10 38)	-311090.370	0.062
33(4 29)-33(3 30)	405942.620	0.021	48(9 40)-47(10 37)	-311096.380	0.001
33(1 32)-32(4 29)	-401873.010	-0.092	50(5 46)-49(6 43)	326660.020	0.004

[a] Transitions below 85 GHz are from ref. 10.

noise mechanism in dc glow discharges is the modulation of the microwave signal as it propagates through a region where the index of refraction is not stable. This noise rapidly decreases with increasing frequency, however, and becomes insignificant beyond 300 GHz. Although the stronger transitions could be observed in real time on an oscilloscope, nearly all measurements were made using source-modulated phase-locked klystrons with lock-in detection at a time constant of one second.

Under the conditions of our experiment, the prior history of the discharge cell (i.e., the wall coatings) substantially affects the CF_2 concentration. If CF_4 is discharged in an initially clean cell, only very weak CF_2 signals are detected. If, however, C_2H_2 is first discharged in the cell for a few minutes to coat the walls with its residue, and pure CF_4 is subsequently discharged, very strong CF_2 lines are observed. We estimate this increase to be more than ×200. From these observations and the very low discharge currents, we conclude that CF_2 is very easy to form in a dc discharge, but that it is also easy to decompose or to lose in a wall reaction. The lifetime of CF_2 in our experiment is approximately one second.

III. RESULTS AND ANALYSIS

CF_2 is a nearly prolate, bent, triatomic asymmetric rotor. The fluorine nuclei occupy identical positions with respect to the symmetry axis of the molecule and the spectrum of CF_2 is, therefore, composed entirely of "*b*" type transitions. In addition, a consideration of the nuclear spin statistics for the two fluorine nuclei

TABLE II

Rotational and Distortion Constants of CF_2 (MHz)

	This Work[a,b]	Kirchhoff et al.[a,b]
A	88355.0879 ± 0.0061	88355.0942 ± 0.066
B	12507.7303 ± 0.0012	12507.5392 ± 0.010
C	10932.2216 ± 0.0012	10932.3151 ± 0.009
Δ_J	$(1.302241 \pm 0.000024)\times10^{-2}$	c
Δ_{JK}	$(-6.76754 \pm 0.0020)\times10^{-2}$	c
Δ_K	2.864946 ± 0.00011	c
δ_J	$(2.197179 \pm 0.00024)\times10^{-3}$	c
δ_K	$(6.81553 \pm 0.0023)\times10^{-2}$	c
H_J	$(1.361 \pm 0.048)\times10^{-8}$	$(1.162 \pm 2.0)\times10^{-7}$
H_{JK}	$(2.568 \pm 0.24)\times10^{-7}$	$(-0.013 \pm 6.0)\times10^{-6}$
H_{KJ}	$(-2.5891 \pm 0.015)\times10^{-5}$	$(-2.555 \pm 5.0)\times10^{-5}$
H_K	$(3.0160 \pm 0.017)\times10^{-4}$	$(3.337 \pm 4.0)\times10^{-4}$
h_J	$(5.958 \pm 0.15)\times10^{-9}$	$(6.60 \pm 20.0)\times10^{-9}$
h_{JK}	$(6.84 \pm 2.6)\times10^{-8}$	$(4.325 \pm 3.0)\times10^{-6}$
h_K	$(3.386 \pm 0.13)\times10^{-5}$	$(-1.580 \pm 1.4)\times10^{-4}$

[a] The errors quoted are for one standard deviations.

[b] The number of significant figures quoted are necessary to reproduce the calculated transition frequencies within their standard deviations.

[c] The τ's of Kirchhoff et al. are not listed since they require further manipulation if they are to be compared with the Watson P^4 parameters.

(*20*) shows that the strength of transitions of the type e ↔ e, o ↔ o, is suppressed by a factor of 3 from transitions of the type e ↔ o, o ↔ e, where e, o refer to the evenness and oddness, respectively, of the pseudoquantum numbers (K_{-1}, K_{+1}).

Table I shows the microwave, millimeter, and submillimeter data that have been obtained for CF_2. Sixty-two new transitions were detected in this work from 85 to 444 GHz. These data included transitions with excitations in excess of 1100 cm^{-1} and have extended the microwave measurements to $J = 50$ and $K = 10$. In addition, the sensitivity of our technique has enabled observation of several transitions that are only weakly allowed. In addition to our results, the eight lines of Powell and Lide (*9*) and thirty-four lines of Kirchhoff *et al.* (*10*) were included in a combined fit. For purposes of analysis these data were weighted according to their estimated experimental error. For the previously available data, the errors estimated in reference 10 were used and for all of our lines an estimate of 0.050 MHz was assumed. We have previously discussed our implementation of Watson's A reduced centrifugal distortion Hamiltonian (*13*, *21*). We have also discussed selection of Hamiltonian terms to be retained in the analysis (*21*) and have found a full set of P^4

and P^6 constants to be appropriate for CF_2. The P^8 terms were tested and found to be unnecessary. Table I also shows the difference between the observed transition frequencies and frequencies calculated from the spectral constants of Table II. Table II also shows the results of Ref. (*10*).

A comparison of the results of Ref. (*10*) with ours shows reasonable agreement although our more recent results are much more accurate. It should be noted that this agreement exists for P^6 constants because all of the constants from the earlier fit are zero to within 2σ. Our constants are in general much smaller than those of Kirchhoff *et al.* Their formulation of the P^4 centrifugal distortion Hamiltonian, while equivalent to ours, is different and does not allow straightforward comparison of terms.

As in other studies of CF_2 (*11*), we observe OCF_2 to be a common impurity. Ordinarily, the high resolution of our technique, the redundancy and accuracy of our analysis, and the relative chemical properties of CF_2 and OCF_2 (the strength of lines due to the latter increase dramatically upon the addition of air to the discharge) allowed us to eliminate impurity lines in a straightforward manner. One line which was removed from the fit is noteworthy. The 1(1, 1)–0(0, 0) transition was measured on two different occasions. Both measurements agreed to within 0.03 MHz but differed by 0.17 MHz from the accurately predicted (σ = 0.008 MHz) transition frequency. Although it did not appear to be an OCF_2 line, this transition had an atypical strength and we concluded that our observations were due to an impurity species other than OCF_2.

The rotational analysis described above allows the calculation of the synthetic spectrum of CF_2. We calculate there to be approximately 850 transitions (including branches that are very weak) below 500 GHz and $J = 50$. All of these are accurately predicted, with most $\lesssim$0.1 MHz. Only a few weakly allowed transitions at high J have uncertainties approaching 1 MHz. Copies of this synthetic spectrum are available from the second author on request.

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