JOURNAL OF MOLECULAR SPECTROSCOPY **118**, 548–549 (1986)

The Millimeter-Wave Spectrum of CF_2Cl_2

Difluorodichloromethane (CF_2Cl_2, Freon-12) is a widely used industrial and commercial chemical. It is commonly used as a refrigerant and as a propellant. Photolysis of this molecule in the upper atmosphere produces Cl ions, which reduce the ozone content of the upper atmosphere (*1*).

Studies of the microwave spectrum have been done previously (*2–4*). Recently Davis *et al.* (*5*) made extensive measurements in the microwave region between 8 and 80 GHz. This large data base allowed them to determine rotational and centrifugal distortion constants, to derive a harmonic force field, and to evaluate ground state structures. In the present work we have extended these measurements into the region between 100 and 300 GHz for the isotopic species $CF_2{}^{35}Cl_2$ and $CF_2{}^{35}Cl^{37}Cl$. The data have been fit to Watson Hamiltonians (*6*) to predict with microwave accuracy the ~10,000 transitions below $J = 60$ in this spectral region.

Details of the millimeter spectrometer that was used in this study have been given previously (*7*). The absorption cell was made of a glass tube 3.65 m long and 10 cm in diameter. Although the millimeter spectrum is dominated by *P*-branch transitions that are doubly degenerate, the observed transitions are weaker than many observed in this region because of the large rotational partition function, the mixture of isotopic species, and the relatively small, 0.51 D (*8*), dipole moment of the molecule.

TABLE I

Observed Transitions

$CF_2{}^{35}Cl_2$			$CF_2{}^{35}Cl^{37}Cl$		
TRANSITION $J'\ K'_a\ K'_c$ – $J''\ K''_a\ K''_c$	FREQUENCY (MHz)	O–C (MHz)	TRANSITION $J'\ K'_a\ K'_c$ – $J''\ K''_a\ K''_c$	FREQUENCY (MHz)	O–C (MHz)
22(21 1)-21(20 2)	176 161.980	-0.016	29(28 1)-28(27 2)	232 112.195	-0.021
22(22 0)-21(21 1)	179 496.009	-0.014	29(29 0)-28(28 1)	235 492.921	-0.056
23(20 3)-22(19 4)	177 720.902	-0.013	30(28 2)-29(27 3)	236 900.175	0.040
23(21 2)-22(20 3)	181 056.686	-0.043	30(29 1)-29(28 2)	240 281.195	0.038
23(22 1)-22(21 2)	184 391.123	-0.023	30(30 0)-29(29 1)	243 661.097	0.100
24(19 5)-23(18 6)	179 274.632	-0.013	31(30 1)-30(29 2)	248 448.999	-0.011
24(20 4)-23(19 5)	182 613.926	0.029	31(31 0)-30(30 1)	251 827.898	0.000
25(17 8)-24(16 9)	177 466.701	0.124	32(31 1)-31(30 2)	256 615.706	-0.031
25(18 7)-24(17 8)	180 818.559	-0.014	54(0 54)-53(1 53)	236 755.534	0.020
25(19 6)-24(18 7)	184 164.218	-0.013	54(1 53)-53(2 52)	238 489.339	0.040
31(30 1)-30(29 2)	250 191.251	0.004	54(2 52)-53(3 51)	240 224.163	-0.014
31(31 0)-30(30 1)	253 517.816	-0.024	54(3 51)-53(4 50)	241 961.202	-0.085
32(29 3)-31(28 4)	251 756.495	-0.015	55(0 55)-54(1 54)	241 118.398	-0.007
32(30 2)-31(29 3)	255 084.707	0.005	55(1 54)-54(2 53)	242 851.886	-0.053
32(31 1)-31(30 2)	258 411.564	0.011	55(2 53)-54(3 52)	244 586.573	0.062
32(32 0)-31(31 1)	261 737.195	0.033	55(3 52)-54(4 51)	246 323.280	0.073
56(0 56)-55(1 55)	250 882.634	-0.014	56(0 56)-55(1 55)	245 481.027	0.025
56(1 55)-55(2 54)	252 623.702	0.024	56(1 55)-55(2 54)	247 214.241	-0.041
56(2 54)-55(3 53)	254 365.663	0.017	56(2 54)-55(3 53)	248 948.534	-0.014
56(3 53)-55(4 52)	256 109.513	-0.025	56(3 53)-55(4 52)	250 684.816	-0.022
56(4 52)-55(5 51)	257 856.599	-0.022	56(4 52)-55(5 51)	252 424.515	0.028
56(5 51)-55(6 50)	259 608.570	0.039	56(6 50)-55(7 49)	255 921.320	-0.022
57(0 57)-56(1 56)	255 341.116	0.000			
57(1 56)-56(2 55)	257 081.865	-0.018			
57(2 55)-56(3 54)	258 823.532	-0.006			

0022-2852/86 $3.00

TABLE II

Rotational Constants

	$CF_2{}^{35}Cl_2$		$CF_2{}^{35}Cl^{37}Cl$	
Constant	Value (MHz)	σ(MHz)	Value (MHz)	σ(MHz)
A	4118.8732	0.00026	4092.0165	0.00086
B	2638.6734	0.00024	2582.2236	0.00067
C	2233.6910	0.00025	2185.4446	0.00061
$\Delta_J \times 10^3$	0.448247	0.000046	0.432155	0.000125
$\Delta_{JK} \times 10^3$	−0.443022	0.000227	−0.437129	0.000399
$\Delta_K \times 10^2$	0.158413	0.000025	0.158322	0.000053
$\delta_J \times 10^3$	0.109411	0.000018	0.105510	0.000044
$\delta_K \times 10^3$	0.133745	0.000277	0.143587	0.000571
RMS Deviation (MHz)		0.029		0.043
Number of independent data points		208		109

The initial predictions for this work were made from an analysis of the data set of Davis *et al.* (*5*). The lines to be measured were selected on the basis of their calculated uncertainties to produce a good analysis and a good set of predictions. The observed frequencies are shown in Table I. Uncertainties in the frequencies measured in this work have been estimated to be ±50 kHz. We have combined our measurements with those of Davis *et al.* (*5*) to produce a new analysis of $CF_2{}^{35}Cl_2$ and $CF_2{}^{35}Cl^{37}Cl$. The techniques used to analyze the data have been discussed in a series of papers on HDS (*9*), HDO (*10*), and D_2S (*11*). Table II shows the results of the new analysis for each isotope. The root-mean-square deviation of the fit for $CF_2{}^{35}Cl_2$ is 29 kHz, while that for the fit to the $CF_2{}^{35}Cl^{37}Cl$ data is 43 kHz. A direct comparison of these constants with those of Davis *et al.* is not possible because of small differences in the terms retained in the Hamiltonians. However, in general the higher frequency transitions reduce the calculated uncertainties by about a factor of 5. The results of these analyses enable us to accurately predict all thermally populated millimeter transitions.

REFERENCES

1. M. J. Molina and F. S. Rowland, *Nature (London)* **249,** 810–812 (1974).
2. H. Takeo and C. Matsumura, *Bull. Chem. Soc. Japan* **50,** 636–640 (1977).
3. C. F. Su and E. L. Beeson, Jr., *J. Chem. Phys.* **66,** 330–334 (1977).
4. H. Jones and M. Morillon-Chapey, *J. Mol. Spectrosc.* **91,** 87–102 (1982).
5. R. W. Davis, M. C. L. Gerry, and C. J. Marsden, *J. Mol. Spectrosc.* **101,** 167–179 (1983).
6. J. K. G. Watson, *J. Chem. Phys.* **45,** 1360–1361 (1966).
7. P. Helminger, F. C. De Lucia, and W. Gordy, *Phys. Rev. Lett.* **25,** 1397–1399 (1970).
8. C. P. Smyth and K. B. McAlpine, *J. Chem. Phys.* **1,** 190–196 (1933).
9. P. Helminger, R. L. Cook, and F. C. De Lucia, *J. Mol. Spectrosc.* **40,** 125–136 (1971).
10. F. C. De Lucia, R. L. Cook, P. Helminger, and W. Gordy, *J. Chem. Phys.* **55,** 5334–5339 (1971).
11. R. L. Cook, F. C. De Lucia, and P. Helminger, *J. Mol. Spectrosc.* **41,** 123–136 (1972).

Randy A. Booker
Frank C. De Lucia

Department of Physics
Duke University
Durham, North Carolina 27706

Received December 23, 1985