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MICROWAVE SPECTRUM AND SUBSTITUTIONAL STRUCTURE OF CH$_2$DF*

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ABSTRACT

Forty-two transitions of the microwave spectrum of CH$_2$DF have been observed in the region between 75 and 450 GHz. The measurement of both a-type and b-type transitions makes possible the analysis of the spectrum and the accurate calculation of the rotational constants (in MHz): $\mathcal{A} = 119\ 675.0535 \pm 0.074$, $\mathcal{B} = 24\ 043.4415 \pm 0.072$, $\mathcal{C} = 22959.3732 \pm 0.072$, $\Delta_J = 0.049371 \pm 0.00011$, $\Delta_{JK} = 0.34268 \pm 0.0006$, $\Delta_K = 1.3774 \pm 0.0035$, $\delta_J = 0.002329 \pm 0.000045$, $\delta_K = 0.0687 \pm 0.036$. These constants, in combination with the results of earlier work on the symmetric species, make possible a r_s structure calculation based entirely on high-accuracy microwave data. The structural parameters are $r_{CH} = 1.100$ Å, $r_{CF} = 1.383$ Å, and $\angle$HCH = 110° 37′.

INTRODUCTION

The methyl halides have been studied both in the IR and microwave spectral regions by a number of workers. However, the relatively high frequencies of the microwave transitions and the complications introduced in the IR spectrum by Coriolis interactions have resulted in substantially less work on methyl fluoride. diLauro and Mills [1] have calculated rotational constants for CH$_3$F and CD$_3$F from IR data and Riter and Eggars [2] have studied the vibrational structure of CH$_2$DF. The symmetric species of methyl fluoride have been studied in the microwave region by several workers [3, 4] and most recently by Winton and Gordy [5].

In this paper we report the results of our study of the nearly prolate symmetric top CH$_2$DF. Because the asymmetry of CH$_2$DF results from a small rotation of the principal axis system of CH$_3$F, weak b-type transitions were observed in addition to the strong a-type "symmetric-top" transitions. As a result $\Delta K_{-1} = 1$ transitions can be measured and the value of the rotational constant calculated directly. The $\mathcal{B}$ rotational constants of the symmetric species and the $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ of CH$_2$DF make possible the calculation of the structural parameters of methyl fluoride. In addition, CH$_2$DF

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represents a test of Watson's reduced centrifugal distortion Hamiltonian [6] in the limit of both large rotational constants and near symmetric-top symmetry ($\kappa = -0.978$).

EXPERIMENTAL PROCEDURE

Many of the transitions which are needed for this study fall in the millimeter and submillimeter region of the spectrum. In addition, the b-type transitions are weak due to the small component of the dipole moment along the b-axis, μ_b. We have previously discussed a sensitive, reliable spectrometer for use in the millimeter and submillimeter region of the microwave spectrum [7]. Briefly, it consists of a klystron-driven crystal harmonic generator, a one-meter quasi-free-space absorption cell, and an InSb photodetector which operates at 1.6 K. Although most of the transitions were strong enough to be observed on an oscilloscope screen, a few were measured on a chart recorder with a lock-in amplifier and a phase locked, slow sweep klystron [8].

The sample for this work was kindly supplied by Professor David F. Eggars of the University of Washington.

THEORY AND ANALYSIS

We have previously discussed the use of Watson's reduced centrifugal distortion Hamiltonian for the analysis of the microwave spectra of asymmetric molecules of the form XY_2(H_2O, [9], etc.), XYZ(HDO [10], etc.) and XYZ_2(ND_2H [11], etc.). For CH_2DF the reduced Hamiltonian has the form

$$\mathscr{H} = \mathscr{H}_r + \mathscr{H}_d{}^{(4)}$$

$$\mathscr{H}_r = \tfrac{1}{2}(\mathscr{B} + \mathscr{C})P^2 + [\mathscr{A} - \tfrac{1}{2}(\mathscr{B} + \mathscr{C})]\,[P_z^2 - b_p P_-^2]$$

$$\mathscr{H}_d{}^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 - \delta_K [P_z^2 P_-^2 + P_-^2 P_z^2]$$

where $P^2 = (P_x^2 + P_y^2 + P_z^2)$ is the total angular momentum, $P_-^2 = (P_x^2 - P_y^2)$, and $b_p = (\mathscr{C} - \mathscr{B})/(2\mathscr{A} - \mathscr{B} - \mathscr{C})$ is Wang's asymmetry parameter for a near prolate top. The large centrifugal distortions of these light, hydrogen containing molecules are a severe test for a centrifugal distortion theory; particularly when the theory is tested to the accuracy of microwave measurements (≈ 0.1 MHz, $0.000003\ \mathrm{cm}^{-1}$). However, none of the light species which have been previously investigated approach the symmetric top limit closely, and it is in this limit that the transformation which results in the reduced Hamiltonian breaks down.

Because the fluorine and carbon nuclei are substantially heavier than the hydrogen nuclei, CH_2DF is only slightly asymmetric. Of light molecules with similar symmetry, only CH_2O [12] and CH_2S [13] have been analyzed by these methods. These molecules are not, however, stringent tests for the breakdown of Watson's transformation in the symmetric top limit because only a-type transitons can be observed in XYZ_2 molecules and the values of $\mathscr{A}$ and Δ_K are difficult to calculate accurately. On the other hand, $\mathscr{A}$ and Δ_K are directly related to the $\Delta_{K_{-1}} = 1$ transitions allowed by the non-zero μ_b of CH_2DF.

Figure 1 shows the importance of these transitions for the accurate calculation of the energy levels and molecular constants of CH_2DF. If only the a-type transitions of a near prolate rotor are observed, then only the "symmetric top" constants $\mathscr{B}$, $\mathscr{C}$, Δ_J and Δ_{JK} can be calculated with accuracy. In order to obtain accurate values for $\mathscr{A}$ and Δ_K, the weak b-type transitions, which define the energy differences between different K_{-1} states, must be observed. Since these are by far the largest constants, any stringent test of distortion theory must be based on data which is sensitive to these constants.

Table 1 shows the 42 microwave transitions measured in this experiment and the transition frequencies calculated from the rotation—distortion constants of Table 2. The calculation of these constants from the observed data has been discussed previously [14]. For Watson's theory to be satisfactory in the near symmetric top limit, it must meet the minimum requirement that the observed data fit the theory to within experimental uncertainty. The r.m.s. deviation between the calculated and observed transition frequencies is 0.074 MHz, which satisfies this condition. Another test for a satisfactory theory is that it predicts accurately unobserved transitions, particularly transitions that are not closely related to the original data set. Table 3 shows several observed transitions that are well beyond the J range included in the analysis and represent, in some cases, different types of transitions. Also shown in Table 3 are transition frequencies calculated from the constants of Table 2 and the corresponding uncertainties. Inspection of this table shows excellent agreement between prediction and observation.

Table 4 lists the ground state energy levels for $J \leqslant 9$ calculated from the molecular constants of Table 2. Since all energy levels can be directly

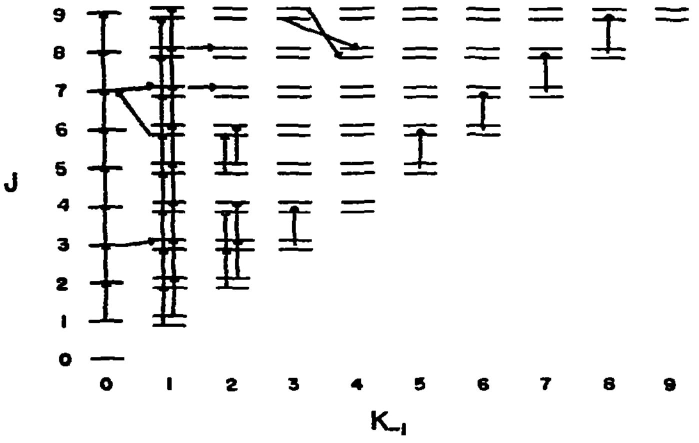

Fig. 1. Energy levels and observed transitions of CH_2DF. Verticle arrows indicate the strong a-type transitions and the angled arrows indicate the weaker b-type transitions.

TABLE 1

Microwave spectrum of CH$_2$DF (MHz)

Transition		Frequency		Obs.—calc.
Upper state	Lower state	Observed	Calculated	
a-Type				
2(0, 2)	1(0, 1)	93 994.872	93 994.895	−0.023
2(1, 2)	1(1, 1)	92 919.018	92 918.960	0.058
2(1, 1)	1(1, 0)	95 086.487	95 086.397	0.090
3(0, 3)	2(0, 2)	140 966.530	140 966.500	0.030
3(1, 3)	2(1, 2)	139 369.908	139 369.928	−0.020
3(1, 2)	2(1, 1)	142 620.694	142 620.756	−0.062
3(2, 2)	2(2, 1)	140 995.003	140 994.887	0.116
3(2, 1)	2(2, 0)	141 031.554	141 031.499	0.055
4(0, 4)	3(0, 3)	187 907.271	187 907.132	0.139
4(1, 4)	3(1, 3)	185 810.754	185 810.753	0.001
4(1, 3)	3(1, 2)	190 144.459	190 144.443	0.016
4(2, 3)	3(2, 2)	187 980.388	187 980.562	−0.174
4(2, 2)	3(2, 1)	188 072.017	188 072.049	−0.032
4(3, 2)	3(3, 1)	187 992.146	187 992.082	0.064
4(3, 1)	3(3, 0)		187 992.371	−0.225
5(0, 5)	4(0, 4)	234 806.509	234 806.565	−0.056
5(1, 5)	4(1, 4)	232 238.116	232 238.168	−0.052
5(1, 4)	4(1, 3)	237 653.866	237 653.790	0.076
6(0, 6)	5(0, 5)	281 654.754	281 654.738	0.016
6(1, 6)	5(1, 5)	278 649.055	278 649.006	0.049
6(1, 5)	5(1, 4)	285 145.060	285 145.038	0.022
6(2, 5)	5(2, 4)	281 916.770	281 916.769	0.001
6(2, 4)	5(2, 3)	282 236.265	282 236.254	0.011
6(5, 2)	5(5, 1)	281 894.034	281 894.136	−0.102
6(5, 1)	5(5, 0)		281 894.136	−0.102
7(0, 7)	6(0, 6)	328 441.934	328 441.893	0.041
7(1, 7)	6(1, 6)	325 040.220	325 040.222	−0.002
7(1, 6)	6(1, 5)	332 614.337	332 614.307	0.030
7(6, 2)	6(6, 1)	328 804.422	328 804.572	−0.150
7(6, 1)	6(6, 0)		328 804.572	−0.150
8(0, 8)	7(0, 7)	375 158.694	375 158.764	−0.070
8(1, 8)	7(1, 7)	371 408.904	371 408.913	−0.009
8(1, 7)	7(1, 6)	380 057.599	380 057.577	0.022
8(7, 2)	7(7, 1)	375 680.627	375 680.717	−0.090
8(7, 1)	7(7, 0)		375 680.717	−0.090
9(0, 9)	8(0, 8)	421 796.865	421 796.834	0.031
9(1, 9)	8(1, 8)	417 752.321	417 752.339	−0.018
9(1, 8)	8(1, 7)	427 470.637	427 470.658	−0.021
9(8, 2)	8(8, 1)	422 517.372	422 517.221	0.151
9(8, 1)	8(8, 0)		422 517.221	0.151
b-Type				
3(1, 2)	3(0, 3)	99 459.274	99 459.230	0.044
7(1, 6)	7(0, 7)	112 206.444	112 206.480	−0.036

TABLE 1 (continued)

Transition		Frequency		Obs—calc.
Upper state	Lower state	Observed	Calculated	
b-Type				
7(0, 7)	6(1, 6)	243 155.209	243 155.212	−0.003
7(2, 5)	7(1, 6)	274 549.303	274 549.327	−0.024
8(2, 6)	8(1, 7)	271 042.504	271 042.485	0.019
8(4, 4)	9(3, 7)	249 721.302	249 721.360	−0.058
8(4, 5)	9(3, 6)	249 676.812	249 676.754	0.058

TABLE 2

Rotational constants of CH_2DF (MHz)[a,b]

$\mathscr{A} = 119\,675.0535 \pm 0.074$; $\mathscr{B} = 24\,043.4415 \pm 0.072$; $\mathscr{C} = 22\,959.3732 \pm 0.072$;
$\Delta_J = 0.049371 \pm 0.00011$; $\Delta_{JK} = 0.34268 \pm 0.0006$; $\Delta_K = 1.3774 \pm 0.0035$;
$\delta_J = 0.002329 \pm 0.000045$; $\delta_K = 0.0687 \pm 0.036$

[a] Errors quoted are twice the statistical standard deviation.

[b] The number of places quoted are required to reproduce the observed microwave lines. Because of the correlations between the constants this number can be larger than the number determined from the uncertainty in the constant.

TABLE 3

Theoretical predictions and observations of high J lines (MHz)

Upper state	Lower state	Predicted frequency (est. uncertainty)[a]	Observed frequency	Obs.— predicted
12(1, 11)	12(0, 12)	144 973.101(0.876)	144 973.151	0.050
11(5, 6)	12(4, 9)	300 716.039(0.502)	300 716.180	0.141
11(5, 7)	12(4, 8)	300 713.328(0.496)	300 713.579	0.251
13(1, 12)	13(1, 13)	98 087.300(1.942)	98 087.564	0.264
15(1, 14)	15(0, 15)	175 978.637(2.72)	175 978.960	0.323

[a] The calculated uncertainties represent two standard deviations in the statistical analysis.

connected to the O_{00} level either by measured transitions or by transitions that can be predicted to within experimental accuracy and since the r.m.s. deviation of the fit is 0.074 MHz, the uncertainty of these energy levels should be $\leqslant 1$ MHz.

STRUCTURE

It is difficult to calculate accurate structural parameters for the methyl halides because only the value of the $\mathscr{B}$ rotational constant can be obtained

TABLE 4

Ground state energy levels of CH_2DF (cm^{-1})

Level	Energy	Level	Energy	Level	Energy
1(0, 1)	1.56784	5(5, 1)	103.67936	8(2, 7)	69.25352
1(1, 1)	4.75770	5(5, 0)	103.67936	8(2, 6)	69.31731
1(1, 0)	4.79385	6(0, 6)	32.90050	8(3, 6)	85.30419
2(0, 2)	4.70317	6(1, 6)	35.74536	8(3, 5)	85.30493
2(1, 2)	7.85714	6(1, 5)	36.50413	8(4, 5)	107.74268
2(1, 1)	7.96559	6(2, 5)	45.74893	8(4, 4)	107.74268
2(2, 1)	17.53449	6(2, 4)	45.77026	8(5, 4)	136.58838
2(2, 0)	17.53480	6(3, 4)	61.78932	8(5, 3)	136.58838
3(0, 3)	9.40531	6(3, 3)	61.78946	8(6, 3)	171.83528
3(1, 3)	12.50602	6(4, 3)	84.23246	8(6, 2)	171.83528
3(1, 2)	12.72291	6(4, 2)	84.23246	8(7, 2)	213.47690
3(2, 2)	22.23758	6(5, 2)	113.08234	8(7, 1)	213.47690
3(2, 1)	22.23910	6(5, 1)	113.08234	8(8, 1)	261.50589
3(3, 1)	38.27413	6(6, 1)	148.33360	8(8, 0)	261.50589
3(3, 0)	38.27413	6(6, 0)	148.33360	9(0, 9)	70.43972
4(0, 4)	15.67321	7(0, 7)	43.85615	9(1, 9)	72.91112
4(1, 4)	18.70400	7(1, 7)	46.58754	9(1, 8)	74.53519
4(1, 3)	19.06544	7(1, 6)	47.59895	9(2, 8)	83.35304
4(2, 3)	28.50793	7(2, 6)	56.71858	9(2, 7)	83.45299
4(2, 2)	28.51251	7(2, 5)	56.75693	9(3, 7)	99.41287
4(3, 2)	44.54487	7(3, 5)	72.76298	9(3, 6)	99.41436
4(3, 1)	44.54488	7(3, 4)	72.76332	9(4, 6)	121.84812
4(4, 1)	66.99072	7(4, 4)	95.20407	9(4, 5)	121.84813
4(4, 0)	66.99072	7(4, 3)	95.20407	9(5, 5)	150.69104
5(0, 5)	23.50552	7(5, 3)	124.05207	9(5, 4)	150.69104
5(1, 5)	26.45063	7(5, 2)	124.05207	9(6, 4)	185.93518
5(1, 4)	26.99272	7(6, 2)	159.30133	9(6, 3)	185.93518
5(2, 4)	36.34520	7(6, 1)	159.30133	9(7, 3)	227.57383
5(2, 3)	36.35588	7(7, 1)	200.94554	9(7, 2)	227.57383
5(3, 3)	52.38328	7(7, 0)	200.94554	9(8, 2)	275.59955
5(3, 2)	52.38332	8(0, 8)	56.37009	9(8, 1)	275.59955
5(4, 2)	74.82797	8(1, 8)	58.97640	9(9, 1)	330.00395
5(4, 1)	74.82797	8(1, 7)	60.27630	9(9, 0)	330.00395

TABLE 5

Methyl fluoride structures

Structure	r_{CH}	r_{CF}	HCH
r_s	1.100 Å	1.383	110° 37′
r_e[a]	1.095 Å	1.382	110° 27′

[a] From ref. 18.

directly from the spectra of CH_3X species. In order to calculate the structure of the methyl group, knowledge of the $\mathscr{A}$ rotational constant, which can be calculated from the spectra of CH_2DX species, is also required. Although there exists considerable literature on the structural calculations of CH_3I, CH_3Br, and CH_3Cl, the complications which result from Coriolis interactions in the IR spectrum and the relatively high frequencies of the microwave transitions have resulted in substantially less work on CH_3F.

Ideally, an equilibrium structure r_e based upon precision microwave data is desired. However, the difficulty associated with the measurement and analysis of the large number of excited states required for this calculation led Costain [15] to propose calculation of a substitution structure r_s. For most purposes, this structure has proven to be more satisfactory than the various ground state structures r_0 that can be calculated directly from the rotational constants. However, Duncan [16] has recently shown that r_s structures of methyl iodide and methyl chloride based on CH_3X/CH_2DX substitution result in CH bonds that are abnormally long when compared to the equilibrium values. In a microwave study Mallinson [17] has confirmed this result for methyl iodide.

From the data presented above for CH_2DF and earlier studies of $^{12}CH_3F$ and $^{13}CH_3F$ [3] the r_s structure of the methyl group can be calculated. As isotopic substitution cannot be performed on fluorine, the C—F bond distance was calculated using the center of mass equation, $\Sigma m_i z_i = 0$. Table 5 shows a comparison between this structure and an equilibrium calculation of Duncan [18]. Inspection of Table 5 shows that unlike the results that have been obtained for the heavier species, the r_s structure of methyl fluoride agrees with the r_e structure to within the experimental uncertainty of the r_e [19].

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REFERENCES

1 C. diLauro and I. M. Mills, J. Mol. Spectrosc., 21 (1966) 386.
2 J. R. Riter, Jr. and D. F. Eggars, Jr., J. Chem. Phys., 44 (1966) 745.
3 O. R. Gilliam, H. D. Edwards and W. Gordy, Phys. Rev., 75 (1949) 1014.
4 S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, J. Chem. Phys., 20 (1952) 1112.
5 R. S. Winton and W. Gordy, Phys. Lett. A, 32 (1970) 219.
6 J. K. G. Watson, J. Chem. Phys., 45 (1966) 1360; 46 (1967) 1935; 48 (1968) 4517.
7 P. Helminger, F. C. de Lucia and W. Gordy, Phys. Rev. Lett., 20 (1970) 1397.
8 F. C. de Lucia, J. Mol. Spectrosc., 55 (1975) 271.
9 F. C. de Lucia, P. Helminger, R. L. Cook and W. Gordy, Phys. Rev. A, 5 (1972) 487.
10 F. C. de Lucia, R. L. Cook, P. Helminger and W. Gordy, J. Chem. Phys., 55 (1971) 5334.
11 F. C. de Lucia and P. Helminger, J. Mol. Spectrosc., 54 (1975) 200.

12 R. B. Nerf, Ap. J., 174 (1972) 467.
13 D. R. Johnson, F. X. Powell and W. H. Kirchhoff, J. Mol. Spectrosc., 39 (1971) 136.
14 R. L. Cook, F. C. de Lucia and P. Helminger, J. Mol. Spectrosc., 41 (1972) 123.
15 C. C. Costain, J. Chem. Phys., 29 (1958) 864.
16 J. L. Duncan, J. Mol. Struct., 22 (1974) 225.
17 P. D. Mallinson, J. Mol. Spectrosc., 55 (1975) 94.
18 J. L. Duncan, J. Mol. Struct., 6 (1970) 447.
19 The equilibrium values of Duncan were calculated from IR values of A_o and B_o and information inferred from the trends of $A_o - A_e$ and $B_o - B_e$ in the other methyl halides. It would appear that since $A_o - A_e$ and $B_o - B_e$ are both small and nearly constant for CH_3I, CH_3Br, and CH_3Cl that the equilibrium structure of methyl fluoride is approximately as accurate as the structure of the other methyl halides. The uncertainties quoted for the other halides are ± 0.004 A for r_{CH} and ± 0.002 A for r_{CX}.