MICROWAVE SPECTRUM, BARRIER TO INTERNAL ROTATION, STRUCTURE, AND DIPOLE MOMENT OF 1,1,1,2-TETRAFLUOROETHANE

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ABSTRACT

The microwave spectrum of CF_3CH_2F has been studied in the 8 to 26 GHz region, with b-type, Q- and R-branch transitions being assigned for the ground vibrational state and first excited torsional state. Relative intensity measurements give a torsional frequency of 108 ± 18 cm⁻¹, which lead to a barrier to internal rotation $V_3 = 3.3 \pm 0.8$ kcal mol⁻¹. The dipole moments determined from the observed first-second order Stark effect are $\mu_a = 0.411 \pm 0.009$ D, $\mu_b = 1.75 \pm 0.22$ D, and $\mu_{total} = 1.80 \pm 0.22$ D. Observed moments of inertia suggest that the CF₃ group is not symmetrical or its axis and the C—C bond are not collinear. The distance $r_{F'\cdots F'}$ is obtained 2.1594 \pm 0.0006 Å, where F' refers to the outer plane fluorine atoms in the CF₃ group.

INTRODUCTION

The microwave spectra have been observed for all of the series of fluorinesubstituted ethanes [1-7] except 1,1,1,2-tetrafluoroethane, CF_3CH_2F . We have therefore examined the microwave spectrum of this molecule to obtain the barrier, structure, and dipole moment, and have compared these properties with related molecules.

EXPERIMENTAL

The 1,1,1,2-tetrafluoroethane was synthesized by the addition of fluorine to the double bond of 1,1-difluoroethene by means of vapor phase reaction with cobalt trifluoride at $125^{\circ}C$ [8]. The sample was purified by gas chromatography and used for the measurement of the microwave spectrum. The microwave spectrometer used was a conventional Stark modulation type [9]. The measurements were made at the temperature of dry-ice except for the relative intensity measurement which was made at room temperature to keep the sample temperature homogeneous.

MICROWAVE SPECTRUM

The spectrum of 1,1,1,2-tetrafluoroethane is an extremely rich one, and consists of groups of lines at intervals of approximately 5 GHz. The central bunches were easily assigned as the Q-branch series of K = 1-2 through K = 3-4 transitions. In the bunch of K = 3-4, a series of strong lines was found and assigned as J = 25 to J = 31 transitions by their intervals and relative intensities. The assignment of the R-branch was, however, rather difficult, because the intensity is much lower than most of the high-J Q-branch lines. The search at Stark voltages of about 20 V where high-J Q-branches are not fully modulated very quickly revealed modulated

TABLE 1

Rotational transitions of 1,1,1,2-tetrafluoroethane in the ground vibrational state and in the first excited torsional state (in MHz)^a

Transition	v = 0		<i>v</i> = 1	
	v _{obs} . ^b	0C	v _{obs} . ^b	0–c
$1_{01} - 2_{12}$	13633.98	0.03	13632.18	0.01
$1_{10} - 2_{21}$	18826.19	-0.10		
$1_{11} - 2_{20}^{11}$	18866.59	0.06	18844.28	0.06
$2_{m}^{2} - 3_{13}^{2}$	19133.00	-0.04	19136.89	0.11
2, -3,	24466,70	0.03	24434.57	0.20
2, -3,	24344.97	-0.06	24331.54	-0.16
2,2-3	14157.14	0.07		
3, -4 4	19771.07	0.08	19745.15	0.08
$3_{03} - 4_{14}$	24612.82	-0.08	24625.46	-0.05

^aOnly *R*-branch transition frequencies are listed. ^b ± 0.1 MHz.

TABLE 2

Rotational constants and centrifugal distorsion constants of CF_3CH_2F in the ground state and in the first torsional excited state^a

	<i>v</i> = 0	<i>v</i> = 1
A(MHz)	5355.631(9)	5349.827(11)
B(MHz)	2799.241(9)	2794.467(11)
C(MHz)	2759.454(9)	2760.789(11)
$\Delta_J(kHz)$	1.10(37)	0.233(44)
$\Delta_{JK}(kHz)$	4.299(3)	4.404(3)
$\Delta_{K}(kHz)$	-4.26(26)	-3.65(28)
$\delta_{J}(Hz)$	-0.66(3)	-1.70(4)
$\delta_{K}(kHz)$	1.430(5)	1.765(7)
fitted lines	112	105

^aStandard deviations, in parentheses, apply to the last significant figure quoted.

R-branch lines. Of the observed lines, only *R*-branch frequencies are listed in Table 1 together with their deviations from the calculated values obtained using the rotational and centrifugal distortion constants given in Table 2. These constants were determined by a least-squares fittings to the 112 observed *R*- and *Q*-branch lines.

The strongest satellite lines in the vicinity of the vibrational ground-state transitions have a similar spectral pattern and were found at slightly lower frequencies than the ground state. These lines were attributed to the first excited state of the torsional oscillation, since this should be by far the lowest frequency vibration of the molecule. The observed frequencies and the deviations from the calculated ones are listed in Table 1. The rotational and centrifugal distortion constants determined by a least-squares fittings to the observed frequencies are shown in Table 2. It should be mentioned that no splitting of any of these spectral lines due to internal rotation was observed. An attempt was made to measure the relative intensities of the ground state and the first excited torsional state transition using the method of Esbitt and Wilson [10]. Twenty-five transitions were investigated but only ten transitions were suitable for the measurement. The difficulties arose from the richness of the spectrum with the consequent complications from Stark lobes of other lines interfering with those being measured. The results for the ten lines which had the least interference are shown in Table 3. The sample temperature was 27°C. The average corresponds to a difference of 108 ± 18 cm⁻¹ in the energies of the two states.

TABLE 3

Intensity ratios of the ground and first excited torsional state of CF₃ CH₂ F

Transition	I(v=1)/I(v=0)		
$17_{2,16} - 17_{3,15}$	0.644		
$22_{2,21} - 22_{3,20}$	0.518		
$24_{2,23} - 24_{3,22}$	0.681		
$27_{2,26} - 27_{3,25}$	0.554		
$28_{2,27} - 28_{3,26}$	0.619		
$29_{2,28} - 29_{3,27}$	0.568		
$30_{2,29} - 30_{3,28}$	0.647		
$31_{2,30} - 31_{3,29}$	0.630		
$26_{3,23} - 26_{4,22}$	0.524		
$30_{3,27} - 30_{4,26}$	0.668		
Average	0.596(50) ^a		

^aStandard deviation, in parentheses, applies to the last significant figure quoted.

MOLECULAR STRUCTURE

A complete structure of 1,1,1,2-tetrafluoroethane cannot, of course, be obtained from the moments of inertia of the normal species. However, a partial structure may be determined and an estimate of the structure with a reasonable degree of certainty can be made.

Initially, it is assumed that the CF₃ group is symmetrical, that the CF₃ axis and the C—C bond are collinear, and that the two hydrogens are equivalent. It is further assumed that $r_{C-H} = 1.090$ Å, \angle CCH = 112.9°, and \angle HCH = 108.9°, the partial structure of fluoroethane [2]. This assumption introduces almost no error since this partial structure is reasonably correct and all of the other atoms are much heavier than hydrogen. By using this partial structure for CH₂ group, the relation

$$J_a + J_b - J_c = m_F r_H^2 \dots r_F + m_H r_H^2 \dots r_H$$

gives the distance of $r_{\rm F...F}$. This relation assumes only that the F-C-C-F framework is coplanar and ignores zero-point vibration. Using 1.7737 ± 0.02 Å for $r_{\rm H...H}$, the error being estimated from related compounds, yields $r_{\rm F...F} = 2.1594 \pm 0.006$ Å. This may be compared with 2.1612 Å obtained for CF₃CH₃ [6]. The $r_{\rm F...F}$ distance places an experimentally determined restriction on the relative values of $r_{\rm C-F}$ and \angle FCC: for example if the value of 1.336 Å is assumed for $r_{\rm C-F}$ then the \angle CCF angle becomes 111.05°. Even with the above assumptions and restrictions, the system is still undetermined. The remaining procedure was to find a set of bond distances and angles which would reproduce the observed moments of inertia subject to the above conditions.

First, as starting values, the bond lengths and bond angles in CH_3CH_2F [2] and CF_3CH_3 [5] were assumed for the corresponding values in CF_3CH_2F . The attempts were made by changing the structural parameters of the heavy atoms; the structure of CH_2 was unchanged throughout the calculation because it has little effect on the moments of inertia. The tentative structural parameters and the differences between observed and calculated moments of inertia are shown as Set I in Table 4. The deviations for I_b and I_c are -0.627 uA^2 and 0.450 uA^2 , respectively. So that we must further change the structural parameters so as to give smaller I_{h} and larger I_{c} . Since the effects of the changes in $r_{C=C}$, $r_{C=F}$, $r_{C=F'}$, $\angle CCF$, $\angle CCF'$, and $\angle CCF''$ on the I_b and I_c are almost the same amount and the same sign, it is impossible to reproduce the observed moments of inertia by changing these parameters under the above conditions. F' and F'' refer to outer plane fluorine atoms in the CF_3 group and to those in the CH_2F group, respectively. Therefore, the structure of the CF₃ group is probably distorted from C_{3v} symmetry or the top axis does not lie on the C-C bond. Two distorted structures for the CF_3 group were considered: one is a tilted structure, i.e. the CF_3 axis and the C-C bond are not collinear, and in the other the angles in the CF_3 group are not symmetrical. The structural parameters which reproduce the

TABLE 4

Parameter	Set I	Set II	Set III
r(C-C)(A)	1.525	1.525	1.525
r(C-F)(A)	1.336	1.336	1.336
r(C-F')(A)	1.336	1.336	1.336
$r(\mathbf{C}-\mathbf{F}'')(\mathbf{A})$	1.345	1.345	1.345
r(C-H)(A)	1.090	1.090	1.090
∠CCF' (°)	111.05	112.11	111.04
∠CCF (°)	111.05	108.91	109.32
$\angle CCF''$ (°)	109.68	109.68	110.40
∠CCH (°)	112.9	112.9	112.9
∠ F ' CF ' (°)	107.85	107.85	107.79
$\angle \mathbf{F}''\mathbf{CH}(^{\circ})$	106.1	106.1	105.62
∠HCH (°)	108.9	108.9	108.9
Tilt angle ^a (°)	0	2.14	
Moments of inertia		$I_{obs} - I_{calc}$	
I_a (u Å ²)	1.033	-0.014	0.017
I_b (u Å ²)	-0.627	0.020	0.009
I_c (u A ²)	0.450	0.009	0.011

Structural parameters of 1,1,1,2-tetrafluoroethane and the deviations between observed and calculated moments of inertia

^aAngle between the CF_3 axis and the C-C bond.

observed moments of inertia are shown as Set II and Set III, respectively, in Table 4. For the former case the tilted angle is 2.14° , and in the latter case the distorted angle in the CF₃ group is a little bit smaller than this. Both sets of structural parameters are essentially the same and are probably close to the actual structure of 1,1,1,2-tetrafluoroethane.

INTERNAL ROTATION

The barrier to internal rotation can be calculated from the observed ratio of the intensities of the ground-state and excited-state transitions. Using the nomenclature of Lin and Swalen [11] the three-fold barrier to internal rotation of the CF₃ group with respect to the CH₂F group is given by $V_3 = 9Fs/4$, where $F = \hbar^2/2rI_{\alpha}$, $r = 1 - \sum_{\alpha} (\lambda_g^2 I_{\alpha}/I_g)$ (g = a, b, c), I_g are the molecular moments of inertia, I_{α} , is the moment of inertia of the CF₃ group around its axis, and the λ_g 's are the direction cosines of the CF₃ axis with the principal molecular axes. The reduced barrier s is obtained, using the tables of Blanch and Rhodes [12], from the difference of the Mathieu eigen-values $\Delta b = b_{\alpha 2} - b_{e0}$ which in turn is related to the observed torsional frequency by $\Delta b = 4 \tilde{\nu}/9F$. The relevant structural and internal-rotational parameters are given in Table 5. The I_{α} and λ values are calculated by using the observed values of the structural parameters of Set II in Table 4. The factor limiting the accuracy

TABLE 5

Internal rotation parameters of 1,1,1,2-tetrafluoroethane and barrier heights of the fluorine-substituted ethanes

$I_{\alpha} = 88.61 \text{ u A}^2$	r = 0.16076
$\lambda_a = 0.8817$	F = 35478 MHz
$\lambda_{b} = 0.4718$	$\Delta b = 40.59$
$\lambda_c = 0$	s = 433
$v = 108(18) \text{ cm}^{-1}$	$V_3 = 3.3(8) \text{ kcal mol}^{-1}$

TABLE 6

Barrier heights of the fluorine-substituted ethanes

Molecule	V_{s} (kcal mol ⁻¹)	Ref.	
CH, CH,	2.882(10)	1	
CH, CH, F	3.31(2)	3	
CH, CHF,	3.199(8)	3	
CH, CF,	3.16(11)	6	
CF, CH, F	3.5(8)	This work	
CF, CHF,	3.51(10)	7	
CF ₃ CF ₃	4.35	14	

of the barrier height, V_3 , is the uncertainty in the intensity ratio measurement. The barrier height determined is 3.3 ± 0.8 kcal mol⁻¹. Danti and Wood [13] reported the barrier height for CF₃CH₂F, from the far-infrared spectrum to be 4.2 ± 0.15 kcal mol⁻¹, we recalculated this barrier height using the structural parameters set II in Table 4 and found a value of 4.0 kcal mol⁻¹. This value is still higher than ours but within the range of uncertainty.

The barrier heights for the molecules formed by the successive substitution of fluorine for hydrogen in ethane are given in Table 6. A deviation from the general trend of fairly invariant barrier height for the CH_3 and CF_3 group with increasing number of fluorine atoms in the framework is observed for CF_3CF_3 .

DIPOLE MOMENT

An effort was made to measure the Stark shift of low-J R-branch lines. For most of cases, because of the richness of the spectrum, it was difficult to follow the Stark lobes up to the high modulation voltages required for Stark shifts large enough to give accurate data. The dipole moments were, therefore, determined from the first-second-order Stark effect of very quickly modulated lines at low Stark voltages where strong Q-branches are not fully modulated. The results obtained for the 2_{12} — 3_{21} transition are given in Table 7. The absorption cell was calibrated using the J = 2-3 transition of OCS, taking the dipole moment of OCS as 0.71521 D [15]. The b-dipole

<i>M</i> = 1			M = 2		
V	$\Delta v_{\rm obs}$.	$\Delta v_{\rm obs}$. $\Delta v_{\rm calc}$.	v	$\Delta v_{\rm obs}.$	$\Delta v_{\rm obs}$. $\Delta v_{\rm calc}$.
0	0.0	0.0	50	6.10	-0.52
50	2.60	0.09	70	9.90	-0.10
70	3.80	0.37	100	15.30	-0.16
100	6.00	-0.51	120	18.70	-0.54
120	8.20	0.10	140	22.70	-0.68
140	9.90	0.11	161	28.30	0.31
161	11.80	0.17	200	36.80	-0.11
180	13.00	0.28			
200	15.00	0.08			
232	17.70	-0.37			
		$\mu_a = 0.411(\pm 0.00)$	9) D		
		$\mu_b = 1.75(\pm 0.22)$	D		
		$\mu_c = 0$ (by symmetry)	etry)		
		$\mu_{total} = 1.80(\pm 0.2)$	2) D		

The Stark shifts (in MHz) for $2_{12}-3_{21}$ transitions and the dipole moments in CF₃CH₂F

TABLE 8

Dipole moments of the related molecules (Debye)

μ	Footnote
1.96(3)	a
2.30(3)	b
2.67(9)	с
2.27(4)	d
1.58(2)	e
1.80(22)	This work
2.8	f
	μ 1.96(3) 2.30(3) 2.67(9) 2.27(4) 1.58(2) 1.80(22) 2.8

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moment was not accurately determined because the Stark shifts caused by the *b*-component of the dipole are small at these Stark voltages.

Dipole moments formed by the successive substitution of fluorine for hydrogen in ethane are given in Table 8. The value $\mu = 1.80 \pm 0.22$ D for CF₃CH₂F is a little lower than the values estimated by the vector addition of those of CH₃CH₂F and CH₃CF₃.





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