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Low Frequency Bands and Barrier to Internal Rotation in Pentafluoroethane

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The infrared absorption spectra of gaseous and liquid CF_3CHF_2 were examined in the region from 500 to 60 cm^{-1}. The Raman spectrum of the liquid at room temperature was also photographed. In the gas-phase spectrum, bands were observed at 414, 363, 306, 246, 216 and 82 cm^{-1}. The contour of the medium-intensity band at 82 cm^{-1} was consistent with that to be expected for torsional oscillation. This frequency would correspond to a triple cosine barrier of 4.4 kcal/mol.

Although infrared and Raman spectra of CF_3CHF_2 have already been studied by Nielsen, Moran and Moran¹⁾ in 1954, the detection and assignment of low frequency bands remain incomplete.

Of low frequency bands, the torsion band, which is expected to be observed as the lowest fundamental, is especially interesting in connection with the barrier height of the internal rotation of the molecule. Ward and Ward²⁾ have pointed out that the barrier height of CH_3CHF_2 was lower than either that of CH_3CH_2F or CH_3CF_3 by 0.2—0.3 kcal/mol, and suggested that, in general, an ethane-like molecule containing the CHX_2 (X: halogen) group might have an abnormally low barrier. Recently, Tipton, Britt and Boggs³⁾ measured the microwave spectrum of CF_3CHF_2, and calculated the torsional frequency 74 cm^{-1}, and the corresponding barrier height 3.51 kcal/mol, on the basis of the relative intensity method. The latter, which was considerably less than either 4.2 kcal/mol for CF_3CH_2F or 4.35 kcal/mol for CF_3CF_3, led us to favor the suggestion of Ward and Ward. Furthermore, Tipton *et al.* mentioned that their calculated torsional frequency 74 cm^{-1}, was in good agreement with the infrared frequency 73.3 cm^{-1},

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1) J. R. Nielsen, H. H. Moran and N. B. Moran, *J. Chem. Phys.*, **23**, 329 (1955).

2) C. R. Ward and C. H. Ward, *J. Mol. Spectr.*, **12**, 289 (1964).

3) A. B. Tipton, C. O. Britt and J. E. Boggs, *J. Chem. Phys.*, **46**, 1606 (1967).

observed by Clague and Danti.[4] However, in the present investigation it was found that the center of the torsion band was located at 82 cm^{-1}, which corresponds to a barrier height of 4.4 kcal/mol, while the absorption maximum of the lower wing was located at 74 cm^{-1} (see Fig. 2). Hence, we reinvestigated the barrier height of the molecule, referring to the theory of Scott and Scheraga[5] concerning the origin of the barrier, and the barrier heights of the chlorine-substituted ethanes reported by Allen, Brier and Lane[6] (see Table 3).

Experimental

The sample of pentafluoroethane, bp −48.5°C, was obtained through the courtesy of Dr. R. J. Plunkett, the E. I. du Pont de Nemours and Company. It was purified by vapor-phase chromatography and dried with phosphorus pentoxide.

The infrared absorption spectra of the gas and the liquid at room temperature were obtained in the region from 500 to 60 cm^{-1} with a Hitachi model FIS-I vacuum, grating, double-beam spectrometer. The gas was contained in a long-path cell built especially for this instrument; its path length was variable in increments of 1.2 m up to 6 m. For the liquid-state spectrum, a polyethylene liquid cell was used, whose effective path length was obscure because of infiltration of the sample into the polyethylene. A spectrum of the sample imprisoned in polyethylene was the same as that of the liquid in the frequency region higher than 200 cm^{-1}, at least, in which the KRS-5 cell could also be used. The Raman spectrum of the liquid at room temperature was photographed with a Yuki-Gosei model RL-II spectrograph of linear dispersion 19 Å/mm at 4358 Å.

All the absorption bands observed are summarized in Table 1. Infrared spectra are shown in Fig. 1.

In order to ascertain the purity of the sample and the correctness of the vibration analysis, an infrared spectrum of the gas between 4000 and 400 cm^{-1} was also obtained with a Perkin-Elmer model 125 grating, double-beam spectrometer.

TABLE 1. FAR INFRARED AND RAMAN SPECTRA OF PENTAFLUOROETHANE
(at room temperature)

Infrared		Raman liquid	Interpretation
Gas	Liquid		
414 m	410 m	413 wd	a'' fundamental
363 m	361 m	362 msh	a' fundamental
306 w	304 m	—	829−523=306 a'
246 s	246 s	250 vw	a' fundamental
216 m	218 m	—	1359−1143=216 a''
82 m	90 m	92 w	a'' fundamental

s : strong, m: medium, w: weak, vw: very weak
wd: weak and diffuse, msh: medium sharp

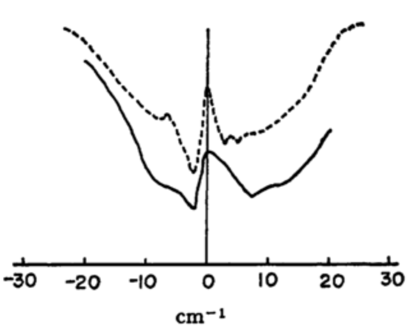

Fig. 2. The contour of the 82 cm^{-1} band.
——: Observed
----: Calculated (with the method of Badger and Zumwalt)

Discussion

Bands in the Region from 500 to 100 cm^{-1}. The CF$_3$CHF$_2$ molecule may be assumed to have the symmetry C_s, and the 18 normal vibrations divide themselves into 11 of species a' and 7 of species a''. In the frequency region lower than 500 cm^{-1}, it is expected that there are two fundamentals for each of the species a' and a''. They are the CF$_3$ symmetric deformation mode, two CF$_3$ degenerate deformation modes, and the torsional mode.

The molecule is an asymmetric top. The principal moments of inertia, calculated from microwave data by Tipton *et al.*,[3] were 136.92, 208.86 and 251.93 amu.Å^2. The axis of the intermediate moment is perpendicular to the symmetry plane. From Badger and Zumwalt's curves,[7] it is found that the a'' fundamentals should have type B contours with a doublet separation of 4.6 cm^{-1}, whereas the a' fundamentals should have contours that are hybrids between type A and C.

In the infrared spectrum of the gas, the medium-intensity band at 414 cm^{-1} has a typical contour of type B and a weak and diffuse counterpart in the Raman spectrum. It is undoubtedly an a'' fundamental. The band at 363 cm^{-1} appears to have PQR structure, and the corresponding Raman band is sharp. It was therefore identified with an a' fundamental. The weak, diffuse and structureless bands at 306 and 216 cm^{-1} had no counterparts in the Raman spectrum. They could be interpreted as difference bands, that is, 829(a')−523(a')=306 cm^{-1}(a') and 1359(a') − 1143(a'')=216 cm^{-1}(a''), respectively. These higher frequency bands were assigned in the present study independently of the previous work by Nielsen *et al.*,[1]

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[4] A. D. H. Clague and A. Danti, Proc. Intern., Symp. Mol. Struct. Spectry. (Columbus Ohio, 1965), to be published.

[5] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965).

[6] G. Allen, P. N. Brier and G. Lane, *Trans. Faraday Soc.*, **63**, 824 (1967).

[7] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

in which the 829 cm^{-1} band was not assigned to any fundamental. Also, Nielsen *et al.* observed a band at 270 cm^{-1}, and assigned it to an a'' fundamental. However, we could detect no absorption band around 270 cm^{-1} in both infrared and Raman spectra. It should be noted that they had no information concerning the purity of their sample.

The population factor for the excited levels of any low frequency fundamental, such as that at 246 cm^{-1}, will be rather large at room temperature. Indeed, the contour of this band has a slightly diffused structure. Its corresponding Raman band at 250 cm^{-1} was weak, but distinct. With somewhat less certainty, it was interpreted as an a' fundamental.

It is well known that in the frequency region higher than 250 cm^{-1}, liquid-phase data is shifted to the lower frequency side of the corresponding vapor-phase data, whereas in the frequency region lower than 250 cm^{-1}, the reverse is the case.[8] Our data also show this feature.

The 82 cm^{-1} Band. This medium-intensity band was only one band that could be detected in the gas-phase infrared spectrum between 120 and 60 cm^{-1}. In the liquid-state data, it was shifted toward a higher frequency of 90 cm^{-1}, and was a comparatively strong band having its Raman counterpart in a weak, diffuse line, at 92 cm^{-1}.

For reference, infrared torsional frequencies for related compounds are collected in Table 2.

The contour of the perpendicular-type torsional fundamental, calculated by the method of Badger and Zumwalt,[7] and shown in Fig. 2, also includes contributions from five "hot bands" which originate from excited vibrational states of the torsion (quantum numbers $v=1, 2, \cdots, 5$). These have a marked effect on the band contour of the torsional frequency, since the population factor $\exp(-h\nu/\boldsymbol{k}T)$ for the excited torsional states is relatively large, and further, the anharmonicity of the cosine potential results in the centers of the hot bands somewhat displaced from that of the $v=0\rightarrow1$. Thus the $v=1\rightarrow2$ band falls 1.2 cm^{-1} below the $v=0\rightarrow1$ band. The rotational structure was expected to be beyond the limit of resolution of the instrument, and no evidence of such structure was found. The observed contour of the 82 cm^{-1} band is consistent with the interpretation of this as the torsional fundamental. Apparently, the absorption minimum of the calculated total band contour resulted in the same wave number as that of the $v=0\rightarrow1$ transition.

For a rough consideration of the intensity of the band, the harmonic oscillator approximation is satisfactory. The dipole moment of the molecule being 1.54 D,[9] it is conjectured that the torsional fundamental will be a band of medium-intensity, or a slightly weaker band than that of CF_3CH_2F (about 2.0 D).

Barrier. Using the method of solving the wave equation for internal rotation,[10,11] the observed torsional frequency 82 cm^{-1}, and the molecular parameters reported by Tipton *et al.*[3] gave a value of 4.4 kcal/mol as the barrier height of the molecule, in which the tables of Blanch and Rhodes[12] were used to obtain the reduced barrier from the difference in the Mathieu's eigenvalues.

The barrier heights for the molecules formed by the successive substitution of fluorine for hydrogen in

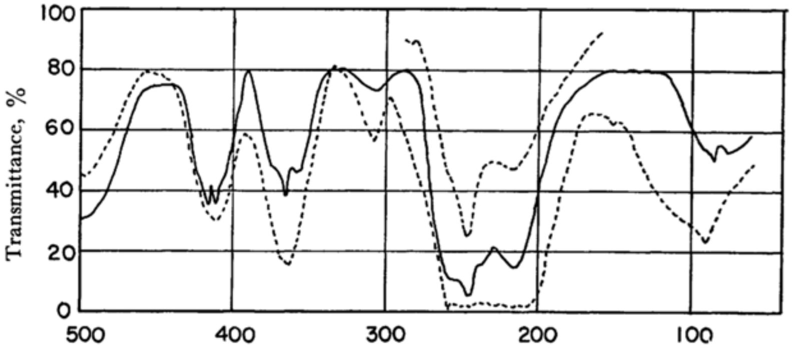

Fig. 1. Far infrared spectra of CF_3CHF_2.

——: Gas, 4.8 m cell, 50 mmHg (room temperature)
----: Liquid, polyethylene cell (room temperature)

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8) G. A. Crowder and D. W. Scott, *J. Mol. Spectr.*, **16**, 122 (1965).

9) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, Inc., New York (1955).

10) D. R. Herschbach, *J. Chem. Phys.*, **31**, 91 (1959).

11) C. C. Lin and J. D. Swalen, *Rev. Mod. Phys.*, **31**, 341 (1959).

12) G. Blanch and I. Rhodes, *J. Wash. Acad. Sci.*, **45**, 166 (1955).

TABLE 2. BARRIER HEIGHTS OF THE FLUORINE-SUBSTITUTED ETHANES

Molecule	Torsional frequency cm^{-1}	V_3 calc.* kcal/mol	V_3 exptl. kcal/mol	Experimental method
CH_3CH_3		3.29	2.87 ± 0.12[a]	Thermodynamic
CH_3CH_2F	241	3.31	3.31 ± 0.02[b]	Microwave
			3.30[c]	Infrared
CH_3CHF_2	235	3.33	3.18 ± 0.01[b]	Microwave
			3.70 ± 0.60[d]	Microwave
			3.2[e]	Infrared
CH_3CF_3		3.35	3.70 ± 0.45[d]	Microwave
			3.5 ± 1.4[f]	Microwave
CF_3CH_2F	120	3.62	4.2[g]	Infrared
CF_3CHF_2	82	4.02	4.4[h]	Infrared
			3.51 ± 0.10[i]	Microwave
CF_3CF_3		4.35	4.35[j]	Electron diffraction

* The values were calculated with the method of Scott and Scheraga.[5]

a) K. S. Pitzer, *Discussions Faraday Soc.*, **10**, 66 (1951).

b) D. R. Herschbach, *J. Chem. Phys.*, **25**, 358 (1956).

c) S. Kinumaki and M. Kozuka, unpublished work.

d) Ref. 5.

e) S. Kinumaki and S. Onodera, unpublished work.

f) H. Mindew and B. P. Dailey, *Phys. Rev.*, **82**, A338 (1951).

g) A. Danti and J. L. Wood, *J. Chem. Phys.*, **30**, 582 (1959).

h) This investigation.

i) A. B. Tipton, C. O. Britt and J. E. Boggs, *J. Chem. Phys.*, **46**, 1606 (1967).

j) E. L. Pace, *ibid.*, **16**, 74 (1948).

TABLE 3. BARRIER HEIGHTS OF THE CHLORINE-SUBSTITUTED ETHANES*

Molecule	V_3, kcal/mol
CH_3CH_3	(3.0)
CH_3CH_2Cl	3.7
CH_3CHCl_2	3.3—3.7
CH_3CCl_3	(2.8) 5.8**
CH_2ClCCl_3	10.0
$CHCl_2CCl_3$	14.2
CCl_3CCl_3	17.5

* All the data were cited from the paper of Allen *et al.*,[6] except the one marked with double stars.

** This value was derived from the cold-neutron study by J. J. Rush (*J. Chem. Phys.*, **46**, 2285 (1967)).

ethane are given in Table 2. In the third column of the table, theoretical values calculated by the method of Scott and Sheraga[5] are listed. In the fourth one, experimental values are collected, which were obtained by each experimental method written in the fifth column.

In the method of calculating the barrier from the infrared or Raman data, it is not taken into account that the infrared torsional frequency is shifted by coupling with other molecular vibrations. Hence, it was checked that, in CH_3CH_2F and CH_3CHF_2, the barrier heights calculated from infrared data were almost equal to those obtained from microwave data. In these molecules, it is supposed that the torsional vibration is quite pure, because the torsional vibrations in the trans configuration of 1,1-dichloro-[13,14] and 1,1-dibromoethane[15] have the potential energy distribution of 90 and 80%, respectively. Consequently, if it may be supposed that the degree of mixing of molecular vibrations is almost equal in CF_3CH_2F and CF_3CHF_2, the experimental barrier heights of these molecules would be as reliable, at least, as the relative values.

According to Scott and Scheraga,[7] the origin of the internal rotation barrier in ethane-like molecules is mainly attributed to two effects, exchange interactions of the electrons in bonds adjacent to the bond about which internal rotation occurs, and nonbonded or van der Waals interactions. They used a modified Buckingham or "6-exp" potential to calculate the nonbonded interaction, and developed a method for obtaining the constants in the 6-exp potential for any pair of atoms based on experimentally available parameters for inert gases. For the exchange interactions, the theory proposed by Pauling was

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[13] T. Miyazawa and K. Fukushima, Preprints for the 16th Annual Meeting of the Chemical Society of Japan (April, 1963), 1S14.

[14] T. Miyazawa and K. Fukushima, *J. Mol. Spectr.*, **15**, 308 (1965).

[15] S. Kanno and T. Miyazawa, Preprints for the 16th Annual Meeting of the Chemical Society of Japan (April, 1964), 1X02.

adopted,[16,17] who showed that, in a molecule of the type $(X_1\ X_2\ X_3)X_4$-$X_5(X_6\ X_7\ X_8)$, U_0, which would be the barrier height in the absence of nonbonded interaction, should be a constant for each class of molecules having the same atoms, X_4 and X_5, regardless of the substitutent atoms X_1, X_2, X_3, X_6, X_7 and X_8. For example, there would be a single U_0 for ethane and all the substituted ethanes, another U_0 for disilane and all its substituted derivatives and another U_0 for acetaldehyde and its halogen derivatives, *etc.* From the above theories, it follows that the difference in the barrier heights of the halogenoethane molecules considered in the present study should be due mainly to the difference in the effects of nonbonded interactions. Since the effect of the H···H nonbonded interaction is comparable to that of H···F and H···Cl in magnitude,[5] both the experimental and theoretical data in Tables 2 and 3 show that the barrier in each of CH_3CHF_2 and CH_3CHCl_2 is almost equal to, or, within the experimental error, slightly less than that of CH_3CH_2F and CH_3CH_2Cl. On the other hand, the X···X (X: F or Cl) nonbonded interaction has an effect so much larger than that of H···H, that either CF_3CHF_2 or CCl_3CHCl_2 has a higher barrier than CF_3CH_2F or CCl_3CH_2Cl. Consequently, we were led to the conclusion that the CHX_2 (X: halogen) group had no unique property; that is, the barrier height of an ethane-like molecule containing this group was not abnormally low, although it is inconsistent with the suggestion by Ward and Ward.[2]

The torsional frequency 74 cm^{-1}, calculated by Tipton *et al.*, and corresponding to a barrier of 3.51 kcal/mol, seems to us to be abnormally low. Here, it should be recalled that their values were calculated by a relative intensity method, which was based on the microwave spectrum of only one kind of isotopic species of the molecule, and frequently led to considerable errors.

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[16] L. Pauling, *Natl. Acad. Sci.* (U. S.), **44**, 211 (1958).

[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York (1960), p. 130.