AIP | The Journal of Chemical Physics

The Infrared Spectrum of CF3D

Santiago R. Polo and M. Kent Wilson

Citation: The Journal of Chemical Physics **21**, 1129 (1953); doi: 10.1063/1.1699149
View online: http://dx.doi.org/10.1063/1.1699149
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/21/7?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 7 JULY, 1953

The Infrared Spectrum of CF_3D

SANTIAGO R. POLO* AND M. KENT WILSON
Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

(Received October 24, 1952)

CF_3D was prepared in high purity and its infrared spectrum investigated. The fundamental frequencies are

$$\nu_1(a_1)=2257\text{ cm}^{-1},\quad \nu_2(a_1)=1111\text{ cm}^{-1},\quad \nu_3(a_1)=693\text{ cm}^{-1},$$
$$\nu_4(e)=1210\text{ cm}^{-1},\quad \nu_5(e)=977\text{ cm}^{-1},\quad \nu_6(e)=502\text{ cm}^{-1}.$$

Thermodynamic functions have been calculated with the usual assumptions.

INTRODUCTION

In relation to an investigation of the absolute intensities of the infrared bands in compounds of the type CX_3H and CX_3D, the compound CF_3D has been prepared and its infrared spectrum studied.

Approximate values of the fundamental frequencies have been calculated,[1] but no reference to the preparation of this substance in isotopic purity nor to any experimental work concerning the vibrational spectrum was found in the literature. Recently the results of a microwave study have been reported.[2]

EXPERIMENTAL

To obtain reliable intensity data it is desirable to have products of high purity. The preparative method described below proved to be completely satisfactory in this respect.

About 4 g of CF_3I from a sample used in a previous investigation[3] was distilled in vacuum and condensed at $-80°C$ into a stainless steel bomb containing 3 g of yellow phosphorus. The bomb was then heated at 250°C for 36 hours.[4] The reaction products were vacuum fractionated into a volatile portion consisting of unreacted CF_3I, a middle fraction consisting in the main of $P(CF_3)_3$ to be used for other purposes, and a final portion consisting of a mixture of $PI(CF_3)_2$ and PI_2CF_3. The final portion was hydrolyzed with a 50 percent solution of sodium deuteroxide in heavy water (99.8 percent D_2O) to yield CF_3D. Traces of unreacted phosphines were easily separated from the product by bulb-to-bulb distillation in vacuum.

The purity of the CF_3D obtained is believed to be very high, as deduced from its infrared spectrum. The strongest band of CF_3H, 1152 cm^{-1}, did not appear at pressures low enough for its observation. At high pressures of CF_3D the strong bands of the deutero compound at 1111 and 1210 cm^{-1} completely obscure the 1150-cm^{-1} region. The second strong band of CF_3H lies at 1372 cm^{-1}. A very weak absorption was observed at 1380 cm^{-1} in the sample of CF_3D, but as the first overtone of the CF_3D fundamental at 693 cm^{-1} might also appear in this region, it is difficult to say whether the sample of CF_3D contained any CF_3H. However, because of the low intensity of the absorption near 1380 cm^{-1} and the characterisitcs of the preparative method, we believe that the ratio of D to H in the product must correspond closely to that of the heavy water used.

Measurements of the infrared spectrum were obtained by means of a Baird Associates spectrophotometer equipped with NaCl optics and a Perkin-Elmer 12 C spectrograph equipped with CaF_2, NaCl, and KBr prisms. Gas cells 5 and 10 cm in length with KBr windows were used.

EXPERIMENTAL RESULTS

The observed frequencies and band assignments are listed in Table I. The observed spectrum replotted on a linear frequency scale is shown in Fig. 1. Since the

TABLE I. Observed frequencies and band assignments for gaseous CF_3D.

ν (cm^{-1})	Assignment	Δ (cm^{-1})[a]
502	$\nu_6(e)$	
693	$\nu_3(a_1)$	
973 981	$\nu_5(e), 2\nu_6(A_1+E)$	27
1111	$\nu_2(a_1)$	
1193	$\nu_6+\nu_3(E)$	2
1210	$\nu_4(e)$	
1378	$(2\nu_3, CF_3H)$?	8
1612	$\nu_2+\nu_6(E)$	1
1671	$\nu_3+\nu_5(E)$	−1
1896	$\nu_3+\nu_4(E)$	7
1948	$2\nu_5(A_1+E)$	6
2078 2090	$\nu_2+\nu_5(E)$	4
2150 2156	$\nu_4+\nu_5(A_1+E)$	36
2257	$\nu_1(a_1)$	
2311	$\nu_2+\nu_4(E)$	10
2412 2429	$2\nu_4(A_1+E)$	0
3256	$\nu_1+\nu_5(E)$	−23
~3360	$\nu_1+\nu_2(A_1)$	~10
~3530	$\nu_2+2\nu_4(A_1+E)$	~0
~3620	$3\nu_4(A_1+E)$	~10

[a] Δ = calc frequency–obs frequency.

---

* Research Fellow of the Spanish National Council for Scientific Research.

[1] Decker, Meister, and Cleveland, J. Chem. Phys. **19**, 784 (1951).

[2] Ghosh, Trambarulo, and Gordy, J. Chem. Phys. **20**, 605 (1952).

[3] S. R. Polo and M. K. Wilson, J. Chem. Phys. **20**, 1183 (1952).

[4] Bennet, Brandt, Emeleus, and Haszeldine, Nature **166**, 225 (1950).

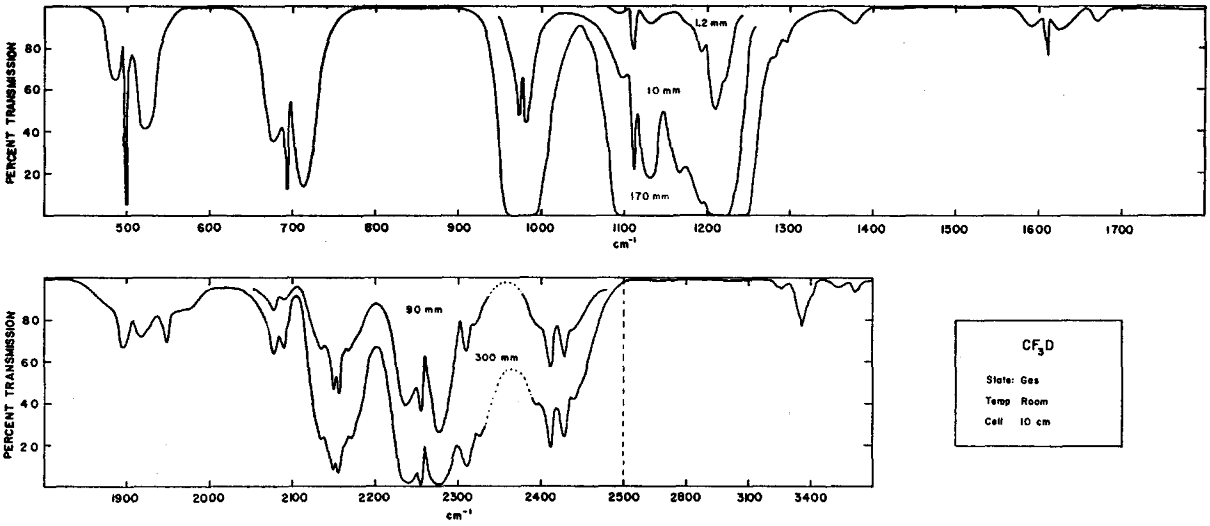

FIG. 1. The infrared spectrum of gaseous CF_3D.

spectra were taken at various pressures and path lengths, the equivalent pressure for a 10-cm path length is indicated in the figure.

DISCUSSION

The assignment of the fundamentals has been made on the basis of the structures and intensities of the bands and by comparison with the assignments previously given for CF_3H,[5,6] which the present investigation supports. There is also good agreement with the predicted frequencies.[1]

The three a_1 fundamental bands have the *PQR* structure characteristic of parallel bands of a symmetric top. The *e*-type fundamental ν_6, at 502 cm⁻¹, also has a *PQR* structure similar to that of a parallel band, indicating that the ζ value is close to $1-I_z/I_x$. The corresponding band in several other symmetric top molecules, for example, CF_3H,[6] NF_3 and PF_3,[7] and BF_3,[8] has this same shape.

The structures of the other two *e*-type bands ν_5 and ν_4 are somewhat more particular. The first, ν_5, shows two clearly resolved peaks of almost the same intensity at 973 and 981 cm⁻¹. Its shape clearly does not correspond to any of the normal band shapes expected for symmetric top molecules.† It is suggested that the observed band shape is the result of Fermi resonance of ν_5 with $2\nu_6(A_1+E)$ whose calculated frequency is 1004 cm⁻¹. Because of the nearly equal intensity of the two peaks of the observed doublet, the two unperturbed levels must be almost coincident. This leads to an anharmonicity for the overtone of about 25 cm⁻¹, which is unexpected in view of the fact that the $2\nu_6$ in CF_3H occurs at exactly twice the frequency of the fundamental.[6] It should be noted that for other overtones and combination bands there is not always correspondence between the two isotopic molecules.

TABLE II. The fundamental frequencies of gaseous CF_3H and CF_3D.

Assignment	ν(cm⁻¹) CF_3H	CF_3D
$\nu_1(a_1)$	3031	2257
$\nu_2(a_1)$	(1152)[a]	1111
$\nu_3(a_1)$	700	693
$\nu_4(e)$	1372	1210
$\nu_5(e)$	(1152)[a]	977
$\nu_6(e)$	507	502

[a] The frequencies ν_5 and ν_2 of CF_3H are somewhat uncertain as these two bands are unresolved.

The strong absorption in the 1200-cm⁻¹ region may be interpreted as the superposition of $\nu_4(e)$, to which the strong peak at 1210 cm⁻¹ may be assigned, and the combination band $\nu_3+\nu_6(E)$. In CF_3H this combination appears as a strong band with a well-defined *PQR* structure. Accordingly, in CF_3D the peak at 1193 cm⁻¹ may be ascribed to the *Q* branch of $\nu_3+\nu_6$; the calculated value is 1195 cm⁻¹. This combination band is rather intense in both molecules, perhaps caused in part by Fermi resonance with the neighboring fundamentals.

In agreement with what has been said about ν_4 and

---

[5] Rank, Shull, and Pace, J. Chem. Phys. **18**, 885 (1950).

[6] E. K. Plyler and W. S. Benedict, J. Research Natl. Bur. Standards **47**, 202 (1951).

[7] M. K. Wilson and S. R. Polo, J. Chem. Phys. **20**, 1716, (1952).

[8] D. M. Gage and E. F. Barker, J. Chem. Phys. **7**, 455 (1939).

† A similar structure has been observed in the *e*-type fundamental at 970 cm⁻¹ of CF_3CH_3 as well as in a number of combination bands involving this fundamental. [Cowan, Herzberg, and Sinha, J. Chem. Phys. **18**, 1538 (1950); Smith, Brown, Nielsen, Smith, and Liang, J. Chem. Phys. **20**, 473 (1952); Nielsen, Claasen, and Smith, J. Chem. Phys. **18**, 1471 (1950)]. The explanation suggested by Cowan, Herzberg, and Sinha is that the doubling results from a splitting of the degeneracy associated with the three potential minima of the torsional mode.

An alternative explanation that can be given is that of a Fermi resonance interaction with the combination of the two low frequency bands, 367+603=970 cm⁻¹. This combination band possesses the required symmetry.

ν_5 the combination bands involving these fundamentals also show a splitting as can be observed in Fig. 1.

A check on the consistency of the assignments is given by the fulfillment of the isotopic relations among the frequencies of CF_3H and CF_3D. From the observed frequencies one obtains

$$\frac{(\nu_1\nu_2\nu_3)_H}{(\nu_1\nu_2\nu_3)_D}=1.407, \quad \text{and} \quad \frac{(\nu_4\nu_5\nu_6)_H}{(\nu_4\nu_5\nu_6)_D}=1.350.$$

The calculated values are 1.404 and 1.375, respectively. The values of the frequencies used in these calculations are those listed in Table II. The moments of inertia I_x are those obtained from microwave data.[2]

Calculation of potential constants are in progress and will be reported in connection with further work on related molecules.

THERMODYNAMIC FUNCTIONS

Thermodynamic functions for CF_3D within a convenient temperature range are listed in Table III.

TABLE III. Thermodynamic functions for CF_3D.[a]

T(°K)	$C_p°$	S°	$\frac{H-H_0}{T}$	$\frac{-(F-H_0)}{T}$
200	10.04	57.82	8.45	49.37
273.15	12.06	61.24	9.14	52.10
298.15	12.76	62.33	9.42	52.91
400	15.40	66.46	10.61	55.84
600	19.08	73.46	12.88	60.59
800	21.25	79.28	14.72	64.56
1000	22.56	84.17	16.17	68.00
1200	23.41	88.37	17.31	71.06
1500	24.18	93.68	18.61	75.06

[a] The units are cal/deg mole.

These values have been calculated for an ideal gas at 1-atmos pressure with a rigid-rotor, harmonic oscillator approximation.

We wish to thank Professor Geoffrey Wilkinson for help with the phosphine preparation and Professor Richard C. Lord, Jr., for helpful discussions. It is also a pleasure to acknowledge a grant-in-aid from the American Academy of Arts and Sciences.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 21, NUMBER 7 JULY, 1953

An Application of Perturbation Theory to the *F* and *G* Matrix Method of Calculating Molecular Vibration Frequencies

P. W. HIGGS
Wheatstone Physics Laboratory, King's College, Strand, London, W.C. 2., England.

(Received February 17, 1953)

The *F* and *G* matrix form of the secular equation for molecular vibrations may be split into two approximate equations, of which one has as its roots the high frequencies (corresponding to relatively rigid bonds, etc.), the other the low frequencies (corresponding to relatively weak bonds, etc.). With the aid of the eigenvectors of these two equations, the exact equation is transformed into a form which yields the corrections to the approximate frequencies by a straightforward application of perturbation theory. The use of the correction terms so derived and the convergence of the perturbation series are illustrated by a discussion of the totally symmetric modes of ethylene.

INTRODUCTION

THE *F* and *G* matrix method introduced by Wilson[1,2] is often useful in the calculation of the vibration frequencies of polyatomic molecules: its chief virtue is that it reduces the order of the secular equation for a molecule containing N atoms from $3N$ to $3N-6$ by eliminating the zero roots which correspond to translation and rotation. In this method the frequencies are obtained from the matrix equation,

$$\mathbf{GFy}_i=\lambda_i\mathbf{y}_i. \tag{1}$$

In this equation

$$\lambda_i=4\pi^2c^2\tilde{\nu}_i^2,$$

where $\tilde{\nu}_i$ is a vibration frequency measured in wave numbers, $\mathbf{y}_i$ is the column vector of internal displacements (extensions of bonds, angular deformations, etc.) in the corresponding normal mode, and **F** and **G** are known symmetric matrices. **F** is the potential energy matrix defined by

$$V=\tfrac{1}{2}\mathbf{y}'\mathbf{Fy},$$

where **y** is a general internal displacement; **G** is the inverse kinetic-energy matrix, such that the kinetic energy of vibration is

$$T=\tfrac{1}{2}\dot{\mathbf{y}}'\mathbf{G}\dot{\mathbf{y}}^{-1}.$$

λ_i is then the ith root of the determinantal equation,

$$|\mathbf{GF}-\lambda\mathbf{I}|=0, \tag{2}$$

where **I** is the unit matrix of order $3N-6$.

(In matrix equations boldface lettering is used to denote matrices, square and rectangular matrices being printed in capitals and row and column vectors in

---

[1] E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939).
[2] E. B. Wilson, Jr., J. Chem. Phys. 9, 76 (1941).