Raman Spectra and Potential Constants for CF$_3$Cl, CF$_3$Br, and CF$_3$I

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(Received October 30, 1953)

Raman frequencies have been obtained for gaseous CF$_3$Cl and CF$_3$Br and for liquid CF$_3$I at −40°C. The assignments are in agreement with previous investigations. The spectra have been analyzed using a simplified, six-constant potential function of the Urey-Bradley type without the assumption of tetrahedral angles around the central carbon atom. In all three cases, it was found possible to reproduce the experimental frequencies to within less than their experimental error.

PREVIOUS workers have reported the infrared[1-6] and Raman[6,7] spectra of the various trifluoromethyl halides. However, in view of the fact that the region of the two lowest fundamentals has been inaccessible in the infrared work and the Raman investigations have dealt with the liquid state, it appears desirable to have information on the gaseous Raman spectra.

Since data have recently become available giving reliable values for bond angles in CF$_3$Cl, it was considered of interest to carry through a vibrational analysis using observed values instead of assuming tetrahedral angles. A Urey-Bradley type of potential function which has not been tried yet with these molecules was selected and calculations were extended to the bromide and iodide for comparison.

EXPERIMENTAL

The spectra were obtained with a Gaertner Raman spectrograph with an $f/3.5$ camera lens. The light source consisted of 12 type AH-11 mercury arc lamps arranged concentrically around the Raman tube and backed by a circular chrome plated reflector. Although this source had been designed primarily for liquid samples, its performance was satisfactory. The gaseous CF$_3$Cl and CF$_3$Br samples were contained in sealed heavy walled Pyrex tubes approximately 18-mm o.d. No internal baffles were used and the background consequently was heavier than desirable on some of the exposures. It was found, however, that the background could be reduced quite appreciably by lengthening the Raman tube and blackening the portion next to the window for several inches. No filters were used for the chloride and bromide but saturated sodium nitrite solution helped to reduce the photochemical decomposition of the iodide.

Both the trifluoromethyl chloride and bromide were supplied by the Jackson Laboratory of E. I. du Pont de

Nemours Company and had been specially purified for PVT work. The iodide was prepared from the silver salt of trifluoroacetic acid[8,9] and purified by bulb to bulb distillation. In all cases, the samples were condensed into the Raman cell after passing through several inches of dried activated alumina followed by an ultrafine Pyrex sintered glass filter. The gas pressures of the bromide and chloride were 6-8 atmospheres. Photochemical decomposition of the vapor made it difficult to obtain the gas spectrum of the iodide and consequently it was obtained only for the liquid state at −40°C.

Exposure times varied from six to forty hours using 103a-J plates. In general, six hours was sufficient to show all fundamentals clearly. Wavelength shifts were measured on tracings made by a Leeds and Northrup microphotometer and the positions of the sharp lines were measured in addition with a comparator. The values reported represent the means of observations from several plates, excitation being by the 4046A, 4358A, and sometimes the 4078A lines of mercury except for the iodide. Semiquantitative polarization data for the iodide were obtained by the two-exposure method using polaroid cylinders.

EXPERIMENTAL RESULTS

The observed frequencies, estimated relative intensities, and assignments are given in Table I.

In general, the standard deviations of the mean for the sharp bands were less than one reciprocal centimeter while those for the broader bands were about two cm^{-1}. The band maxima were measured in all cases. The

TABLE I. Observed Raman frequencies in cm^{-1} for CF$_3$Cl, CF$_3$Br, and CF$_3$I.

CF$_3$Cl (gas)		CF$_3$Br (gas)		CF$_3$I (liq.)		
Freq.	Assign.	Freq.	Assign.	Freq. (cm^{-1})	Assign.	Pol.
351 w, br	ν_6 e	305 w, br	ν_6 e	267 w, br	ν_6 e	$\cdots$
475 s	ν_3 a_1	350 s	ν_3 a_1	285 vs	ν_3	pol.
559 w, br	ν_5 e	549 w, br	ν_5 e	541 w, br	ν_5 e	dp.
782 s	ν_2 a_1	762.5 s	ν_2 a_1	739 s	ν_2	pol.
1104 ms, br	ν_1 a_1	1081 ms, br	ν_1 a_1	1058 mw, br	ν_1 a_1	pol.
1217 w, br	ν_4 e	1209 w, br	ν_4 e	1177 w, br	ν_4 e	dp.
				1024 vw	$\nu_2+\nu_3$ A_1	$\cdots$

[1] H. W. Thompson and R. B. Temple, J. Chem. Soc. 1948, 1422.

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

[3] E. K. Plyler and N. Acquista, J. Research Natl. Bur. Standards 48, 92 (1952).

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

[5] McGee, Cleveland, Meister, Decker, and Miller, J. Chem. Phys. 21, 242 (1953).

[6] W. F. Edgell and C. E. May, J. Chem. Phys. 20, 1822 (1952).

[7] L. Kahovec and J. Wagner, Z. physik. Chem. B48, 188 (1941).

[8] A. L. Henne and W. G. Finnegan, J. Am. Chem. Soc. 72, 3806 (1950).

[9] Hauptschein, Nodiff, and Grosse, J. Am. Chem. Soc. 74, 1347 (1952).

assignments given above are in agreement with those previously proposed[4-6] and are further substantiated by the nature of the bands. With the exception of ν_1, all A_1 bands showed a sharp and intense Q branch, while the E bands were much weaker and of a broad and diffuse character. The ν_1 band associated with the symmetrical stretching motion of the fluorine atoms was an exception, being rather broad, only moderately intense, and without the pronounced Q branch observed for the other A_1 frequencies. Similar observations have been made by J. Rud Nielsen and others for symmetrical fluorine stretching motions in other molecules. The semiquantitative polarization data for CF₃I also are in agreement with previous assignments and do not agree with the suggestion by Pitzer and Gelles[10] that the values for ν_3 and ν_6 be interchanged.

FORCE CONSTANT TREATMENT

The vibrational spectra of these molecules have been analyzed previously[5,11] using valence force coordinates and a complete quadratic potential function. However, the simplicity and ease of interpretation of the Urey-Bradley type of potential field favor its use in those cases where it can be applied successfully; it has been found particularly suitable for halogenated methane derivatives.[12,13] In the present case, a simplified potential function of this type containing only six force constants, the same as the number of vibrational frequencies, was found adequate to reproduce all of the observed data.

The potential function employed for the CF₃X molecule is

$$2V = k_R\Delta R^2 + k_r\sum\Delta r_i^2 + k_\alpha\sum(r\Delta\alpha_i)^2 + k_\beta\sum(r\Delta\beta_i)^2 + k_D\sum\Delta D_i^2 + k_d\sum\Delta d_i^2, \quad (1)$$

where R represents the $C-X$ distance, r the $C-F$ distance, D the $X-F$ distance, d the $F-F$ distance, α the $F-C-F$ angle, and β the $F-C-X$ angle. Since these coordinates are not all independent, the potential energy expression was converted to a form involving bond angles and distances alone by means of the following relationships:

$$\Delta D_i = \frac{1}{D}[(r_i - R\cos\beta_i)\Delta r_i + (R - r_i\cos\beta_i)\Delta R + r_i R\sin\beta_i\Delta\beta_i], \quad (2)$$

$$\Delta d_{ij} = \sin\frac{\alpha_{ij}}{2}\Delta r_i + \sin\frac{\alpha_{ij}}{2}\Delta r_j + (r_i + r_j)/2\cos\frac{\alpha_{ij}}{2}\Delta\alpha_{ij}. \quad (3)$$

These expressions are adequate to a first degree of approximation. The analysis was made by the familiar $F-G$ matrix method of Wilson, the symmetry coordinates employed being identical with those chosen by

TABLE II. Molecular parameters for CF₃Cl, CF₃Br, and CF₃I used in force constant calculations.

	CF₃Cl[a]	CF₃Br	CF₃I
$C-F$ dist.	1.328 A.U.	1.328 A.U.	1.332 A.U.
$C-X$ dist.	1.753	1.918	2.134
$\angle F-C-F$	108° 42'	108° 25'	108° 0'
$\angle F-C-X$	110° 18'	110° 31'	110° 55'
$F-F$ dist.	2.158	2.154	2.155
$F-X$ dist.	2.540	2.688	2.891

[a] Reference 15. Atomic weights (phys. scale):

C = 12.0039	F = 19.0045	I = 126.932
Cl = 34.9787	Br = 79.941	

Avogadro's number: $N = 6.02544 \times 10^{23}$ (DuMond and Cohen, 1951).

Meister and Cleveland.[14] The elements of the symmetry factored F matrix are given below:

$$F_{11} = k_R + 3k_D A^2,$$

$$F_{12} = 3^{\frac{1}{2}}k_D AB,$$

$$F_{13} = -(3/2)^{\frac{1}{2}}rRk_d AC,$$

$$F_{22} = k_r + 4k_d\sin^2\alpha/2 + k_D B^2,$$

$$F_{23} = 2^{-\frac{1}{2}}rk_d\sin\alpha - 2^{-\frac{1}{2}}rRk_D BC,$$

$$F_{33} = \frac{1}{2}r^2[k_\alpha + k_\beta + k_d\cos^2\alpha/2 + R^2k_D C^2],$$

$$F_{44} = k_r + k_d\sin^2\alpha/2 + k_D B^2,$$

$$F_{45} = rRk_D BC,$$

$$F_{46} = -\frac{1}{2}rk_d\sin\alpha,$$

$$F_{55} = r^2k_\beta + r^2R^2k_D C^2,$$

$$F_{56} = 0,$$

$$F_{66} = r^2k_\alpha + r^2k_d\cos^2\alpha/2,$$

$$A = \frac{(R - r\cos\beta)}{D}, \quad B = \frac{(r - R\cos\beta)}{D}, \quad C = \frac{\sin\beta}{D}.$$

Practically all normal coordinate treatments of methane derivatives carried out up to now have assumed tetrahedral angles around the central carbon atom. Electron diffraction and infrared investigations have shown that, in some cases, deviations from the tetrahedral figure may be appreciable. A recent sector electron diffraction investigation by Dr. L. S. Bartell[15] has furnished reliable values for all the parameters of CF₃Cl. Although microwave data are available for both CF₃Br and CF₃I, the situation is not quite as satisfactory since it was necessary to assume values for at least one of the molecular parameters in each case in order to calculate the rest. Unequivocal values for the angles consequently could not be obtained. For the purpose of these calculations, suitable values for the angles in CF₃Br and CF₃I were chosen to be consistent with the microwave data and to reflect the increased steric effect to be expected for the Br and I atoms as compared to Cl. The numerical values of the various parameters are listed in Table II.

[10] K. S. Pitzer and E. Gelles, J. Chem. Phys. 21, 855 (1953).
[11] Decker, Meister, and Cleveland, J. Chem. Phys. 19, 784 (1951).
[12] T. Simanouti, J. Chem. Phys. 17, 245 (1949).
[13] T. Simanouti, J. Chem. Phys. 17, 848 (1949).
[14] A. G. Meister and F. F. Cleveland, Am. J. Phys. 14, 13 (1946).
[15] L. S. Bartell and L. O. Brockway (to be published).

TABLE III. Calculated and observed values for the vibrational frequencies of the trifluoromethyl halides (in cm^{-1}).

CF$_3$Cl		CF$_3$Br		CF$_3$I	
Obs	Calc	Obs	Calc	Obs[a]	Calc
1104	1104	1081	1081	1074	1074
782	782	762.5	762.2	741	741
475	475	350	350	285	285
1217	1217	1209	1209	1185	1185
559	559	549	549	540	540
351	351	305	305	264	264

[a] Selected as most probable values from the infrared measurements on CF$_3$I vapor. References 3, 4, 5, and 6.

TABLE IV. Force constants for the trifluoromethyl halides.

	($\times 10^{-5}$ dynes/cm)		
	CF$_3$Cl	CF$_3$Br	CF$_3$I
k_R	2.977	2.596	2.593
k_r	4.528	4.596	4.420
k_α	0.531	0.426	0.456
k_β	0.305	0.345	0.352
k_d	1.168	1.368	1.241
k_D	0.732	0.465	0.209

Expressions for the inverse kinetic energy matrix elements in terms of bond distances and atom masses have been tabulated by Decius for nontetrahedral angles.[16] These were evaluated and the inverse kinetic energy matrix transformed to the symmetry factored G matrix. The values of the force constants were then systematically adjusted as usual until the roots of the secular equation, $|FG - \lambda I| = 0$, coincided with the experimental values. No attempt was made to transfer force constants from one molecule to another. In all three cases, it was possible to obtain agreement to within less than one wave number of the experimental values as shown in Table III. The force constants are listed in Table IV.

The good agreement between the observed and calculated frequencies obtained with such a simple potential function gives additional emphasis to the usefulness of the Urey-Bradley type of field. The success achieved in this case cannot be considered particularly unusual, however, since central force fields have in the past been most successful with completely halogenated methane derivatives. The present disfavor of such fields has been chiefly due to their inadequacy when hydrogen atoms

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[16] J. C. Decius, J. Chem. Phys. 16, 1025 (1948).

are present in the molecule, and in this connection it is interesting to speculate whether the fit obtainable might not be improved by the use of correct angle parameters instead of assuming tetrahedral. No indication of this was given in the present work since the CF$_3$Cl frequencies could be fitted equally well using either observed or tetrahedral angles. The effect of this change in parameters on the force constants is shown in Table V. Similar calculations were not carried out for the other two molecules.

Inspection of the force constants in Table IV shows that those constants primarily associated with the CF$_3$ group, k_r, k_α, and k_d, have approximately the same values in all three molecules indicating that the CF$_3$ radical is little affected by the particular halogen to which it is attached. The remaining three constants, as might be expected, vary systematically as the halogen is changed from Cl to Br to I. A more detailed comparison does not seem warranted in view of the uncertainty in the angle values in the bromide and iodide and the lack of information on the anharmonicities.

ACKNOWLEDGMENT

TABLE V. Effect of angle parameters on force constants of CF$_3$Cl.[a]

	Observed angles	Tetrahedral angles	Difference
k_R	2.977	3.197	7.4%
k_r	4.528	4.453	-1.7
k_α	0.531	0.562	5.8
k_β	0.305	0.311	2.0
k_d	1.168	1.070	8.4
k_D	0.732	0.730	-0.3

[a] Force constants in 10^5 dynes per centimeter.

Note added in proof:—The Raman spectrum of gaseous CF$_3$Cl has been reported quite recently by H. H. Claassen [J. Chem. Phys. 22, 50 (1954)] while the present article was in press. The agreement between the two sets of experimental data for this molecule is excellent. Claassen in addition observed ν_3 for the Cl^{37} isotopic species, the shift being 7.6 cm^{-1} from the value for the Cl^{35} species. This may be compared with a shift of 6.8 cm^{-1} calculated from the present treatment.