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Raman Spectra and Vibrational Assignments for 1,1,1-Trihaloethanes and Their Deuterium Derivatives

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Raman spectra of the first three members of the 1,1,1-trihaloethane series, CH_3CX_3, X = F, Cl, Br, were obtained for the liquids under low resolution. All but two active fundamental vibrational frequencies were observed, and for most bands it was possible to make a qualitative determination of the depolarization ratio. The completely deuterated compounds were synthesized and their spectra also were examined. Normal coordinate calculations were carried out to confirm the proposed assignments.

INTRODUCTION

Vibrational spectra of only two 1,1,1-trihaloethanes have been reported in the literature. The fluorine compound, CH_3CF_3, has been studied by a number of investigators (*1–5*) with general agreement in assignments except for the two CF_3 deformation modes where uncertainty as to symmetry species exists. The only reference to the deuterated variety is in a recent article by Lafon and Nielsen (*6*) who cite values for the fundamentals based on data in a dissertation by Susi (*7*). No experimental details are given in Ref. (*6*).

The infrared and Raman spectra of 1,1,1-trichloroethane have been reported by numerous workers and only the most recent articles are cited here (*8–12*). The assignments for this molecule were the subject of controversy for some time until Evans and Bernstein (*12*) resolved the remaining uncertainty with the help of the spectrum of the deuterated molecule. The assignments for this molecule appear well established.

Vibrational data for the little known compound 1,1,1-tribromoethane have never been reported.

The only recent normal coordinate analysis of these molecules is the treatment by Lafon and Nielsen (*6*) of CH_3CF_3 and CD_3CF_3 using a Urey-Bradley potential function. Earlier calculations (*10, 13*) were based on incomplete data and also have been shown to contain errors (*6, 14*).

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EXPERIMENTAL METHODS

The 1,1,1-trifluoroethane was prepared by halogen exchange between CH_3CCl_3 and SbF_3 using a small amount of SbF_3Cl_2 as a halogen carrier. The method was essentially that of Henne and Renoll (*15*). The product was purified by repeated bulb-to-bulb distillation until its infrared spectrum showed no further change. The deuterated fluoride was prepared in the same manner starting with 1,1,1-trichloroethane-d_3.

The 1,1,1-trichloroethane was obtained from Distillation Products Industries, Inc., and distilled through a small fractionating column before use. Its spectrum was in good agreement with published records. The authors are indebted to Dr. L. C. Leitch of the Canadian National Research Council for an initial sample of 1,1,1-trichloroethane-d_3. Additional material was prepared by a method similar to that of Francis and Leitch (*16*) using trichloroethylene as starting material.

The only synthesis of 1,1,1-tribromoethane found in the literature was based on a Wurtz reaction between CH_3Br and CBr_4 (*17*). Since this method gave poor yields of a product which was difficult to purify, a new and improved method was developed in the present work which is described as follows. Five ml of CH_3CCl_3 were dissolved in 250 ml of carbon disulfide previously saturated with HBr at 0°C. A solution of 4 g of anhydrous $AlBr_3$, dissolved in 100 ml of dry CS_2 in a dropping funnel, was added dropwise to the CH_3CCl_3 solution over the course of an hour. During the addition, a slow stream of HBr was passed through the reaction mixture. To recover the product, the reaction mixture was extracted twice with ice water made basic with ammonium hydroxide. After drying, the solvent was distilled off and the residue was vacuum distilled (bp 60–70°C at 15 mm Hg). Further purification was carried out by repeated fractionation on the vacuum line, the final yield being about 50%. The identity of the compound was established by its mass spectrum and chemical analysis for total halogen; calc for Br, 89.9%; found, 89.8%. 1,1,1-Tribromoethane is a white solid with a melting point of 30°C. It is decomposed by light when impure but the pure material is quite stable and remains colorless indefinitely when sealed off in glass in the absence of oxygen. The deuterated bromide was prepared in the same fashion starting with the deuterated chloride.

Samples for spectroscopic examination were prepared by distilling the compounds into capillary Raman tubes which were then sealed off under vacuum. The spectrograph and light source have been described previously (*18*). Spectra were obtained with the samples in the liquid state, the temperatures being 0° for the fluoride, 25° for the chloride and 40° for the bromide. Qualitative estimates of the depolarization ratios were obtained using the two-exposure method and polarizing the incident light with Polaroid cylinders. Several plates were taken for each compound and measurements were made both on plates and on

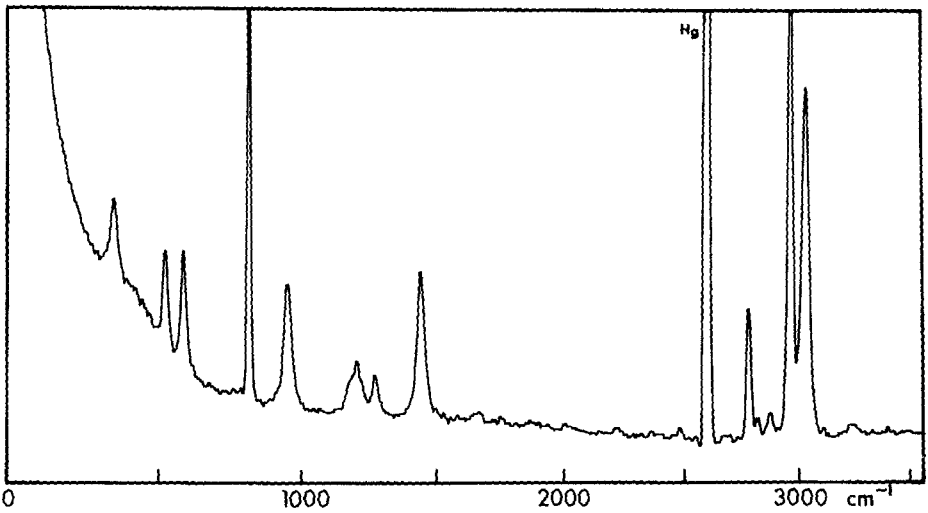

FIG. 1. Raman spectrum of liquid CH_3CF_3 at 0°C

microphotometer tracings. The data tabulated represent weighted averages of all measurements for a particular compound.

EXPERIMENTAL RESULTS AND ASSIGNMENTS

Apparently the only one of these molecules for which a fully determined structure has been published is the fluoro compound (*19*, *20*). However, there seems little doubt that the CH_3CX_3 molecules have C_{3v} symmetry with a staggered configuration. This model predicts 12 fundamental frequencies with the distribution $5A_1 + A_2 + 6E$, the A_2 frequency being both Raman and infrared inactive. The numbering scheme and approximate description of fundamentals for all three molecules follows that used previously for CH_3CCl_3 (*8*). Although as a result the numbering of some of the CH_3CF_3 fundamentals becomes inconsistent with previous work and the usual conventions, the series itself is internally consistent.

1,1,1-Trifluoroethane. Microphotometer tracings of the Raman spectra of 1,1,1-trifluoroethane and its deuterated derivative are shown in Figs. 1 and 2 while the observed Raman fundamentals are listed in Tables I and II. Assignments and frequency values for both compounds agree with those given by Nielsen (*6*) and Susi (*7*). A few of the bands appear to be sensitive to physical state, for example the bands near 800 cm^{-1} where the Raman (liquid) and infrared (gas) values differ somewhat. In the early work on CH_3CF_3 (*4*, *5*), disagreement existed as to the relative assignment of the two CF_3 deformation modes since the depolarization ratios of the two bands are about the same. The present work on the deuterated compound shows that the higher of the

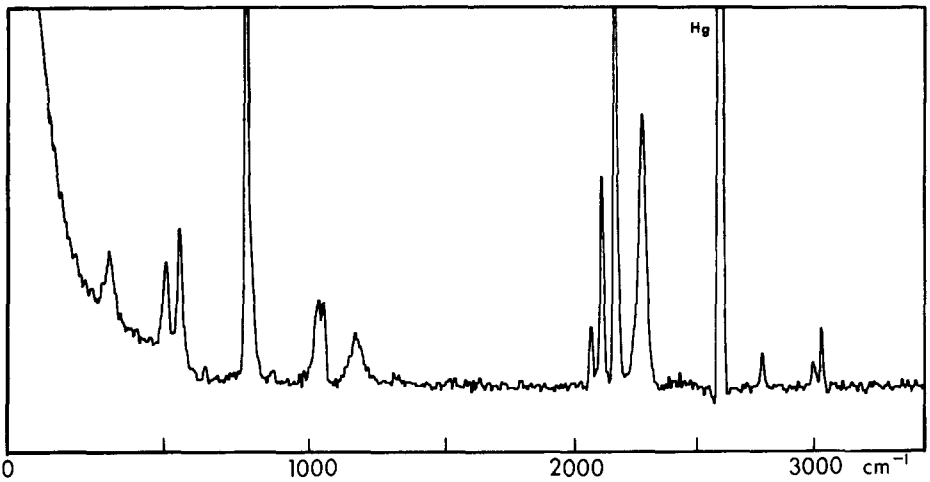

FIG. 2. Raman spectrum of liquid CD_3CF_3 at 0°C

TABLE I

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES FOR CH_3CX_3 MOLECULES (X = F, Cl, Br) (in cm^{-1})

Freq. no. and descript.	CH_3CF_3			CH_3CCl_3			CH_3CBr_3		
	Obs	Calc	Δ	Obs	Calc	Δ	Obs	Calc	Δ
A_1 Class									
ν_1 ν C–H	2970	2971	−1	2943	2943	0	2938	2938	0
ν_2 δ CH_3	1408	1410	−2	1384	1384	0	1373	1373	0
ν_3 ν C–C	827	829	−2	1071	1071	0	1045	1045	0
ν_4 ν C–X	1282	1285	−3	525	526	−1	408	407	1
ν_5 δ CX_3	600	602	−2	343	342	1	211	211	0
E Class									
ν_7 ν C–H	3038	3041	−3	3009	3011	−2	2993	2994	−1
ν_8 δ CH_3	1452	1452	−1	1444	1450	−6	1432	1434	−2
ν_9 ρ CH_3	963	962	1	1079	1079	0	1064	1060	4
ν_{10} ν C–X	1214	1212	2	711	713	0	628	623	5
ν_{11} δ CX_3	538	540	−2	343	344	−1	275	279	−4
ν_{12} ρ CX_3	366	369	−3	238	239	−1	145	144	1

two bands clearly is polarized and the lower is not giving an unequivocal assignment. Since it seems unlikely that the symmetric and asymmetric motions would interchange position upon deuteration, the evidence supports Nielsen's assignment of the higher band to the symmetric mode in CH_3CF_3.

In the case of CD_3CF_3, only four clearly polarized bands of medium to high intensity were observed and the location of the fifth A_1 fundamental proved

TABLE II

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES FOR CD_3CX_3 MOLECULES (X = F, Cl, Br) (in cm^{-1})

Freq. no. and descript.	CD_3CF_3			CD_3CCl_3			CD_3CBr_3		
	Obs.	Calc.	Δ	Obs.	Calc.	Δ	Obs.	Calc.	Δ
A_1 Class									
ν_1 ν C–D	2170	2169	1	2130	2130	0	2116	2116	0
ν_2 δ CD_3	1065	1062	3	1142	1142	0	1110	1110	0
ν_3 ν C–C	798	795	3	975	975	0	953	953	0
ν_4 ν C–X	1322	1320	2	504	503	1	388	389	−1
ν_5 δ CX_3	568	566	2	332	333	−1	209	210	−1
E Class									
ν_7 ν C–D	2281	2277	4	2259	2256	3	2241	2239	2
ν_8 δ CD_3	1182	1184	−2	1050	1042	8	1038	1035	3
ν_9 ρ CD_3	820	822	−2	914	915	−1	883	887	−4
ν_{10} ν C–X	1045	1043	2	654	654	0	583	589	−6
ν_{11} δ CX_3	522	524	3	316	315	1	244	240	4
ν_{12} ρ CX_3	332	328	4	231	230	1	142	142	0

somewhat elusive. Application of the product rule (Table III) predicted that the missing band should be located around 1300 to 1350 cm^{-1}. On long exposures, a weak band was finally observed in this region with its maximum at about 1322 cm^{-1} and this is assigned to the missing fundamental. Its polarization state could not be determined due to its low intensity but the product rule does not allow any other choice. Susi (*7*) states that the infrared intensity of this band is fairly high as is customarily observed in modes involving a CF_3 group. The unexpectedly high frequency position is attributed to the influence of another A_1 fundamental nearby at 1065 cm^{-1}; as might be expected, the normal coordinate calculations show that the 1322 cm^{-1} mode is strongly mixed.

A somewhat similar situation was found in the E class frequencies of CD_3CF_3; examination of the spectrum yielded only five depolarized bands that could be readily assigned by comparison with the hydrogen compound. The missing frequency was ν_9 which the product rule indicated should be found in the neighborhood of 850 cm^{-1}. Careful inspection of the plates and tracings revealed a weak band nearly obscured by the strong peak due to an A_1 fundamental at 798 cm^{-1}. This band, which is visible as a weak shoulder in the tracing of Fig. 2, is assigned to the missing fundamental. The estimated position of 820 cm^{-1} may be slightly high since Susi (*7*) gives values of 805 and 798 cm^{-1} for the A_1 and E fundamentals, respectively.

1,1,1-Trichloroethane. The Raman spectra of the normal and deuterated compound were obtained in the present investigation largely as a matter of completeness and to provide comparison spectra. The assignment of fundamentals given by Evans and Bernstein (*12*) was confirmed. Their explanation

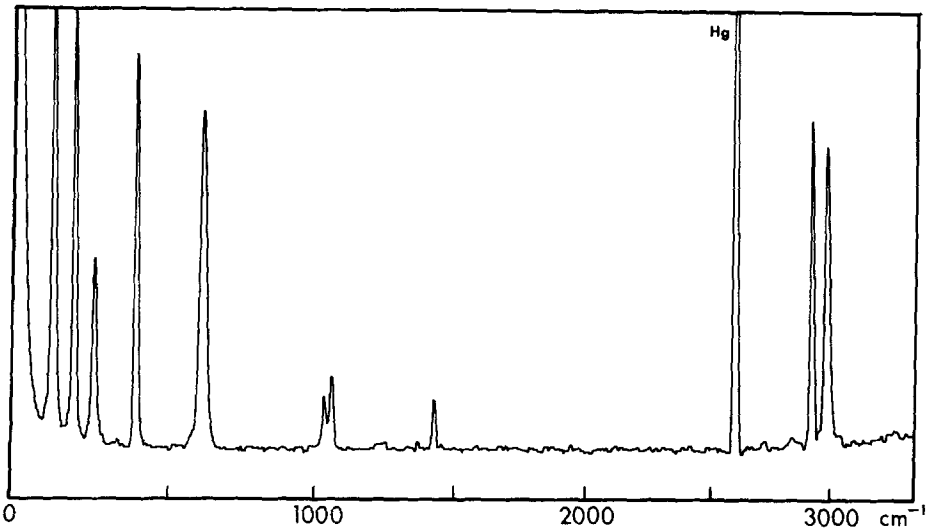

FIG. 3. Raman spectrum of liquid CH_3CBr_3 at 40°C

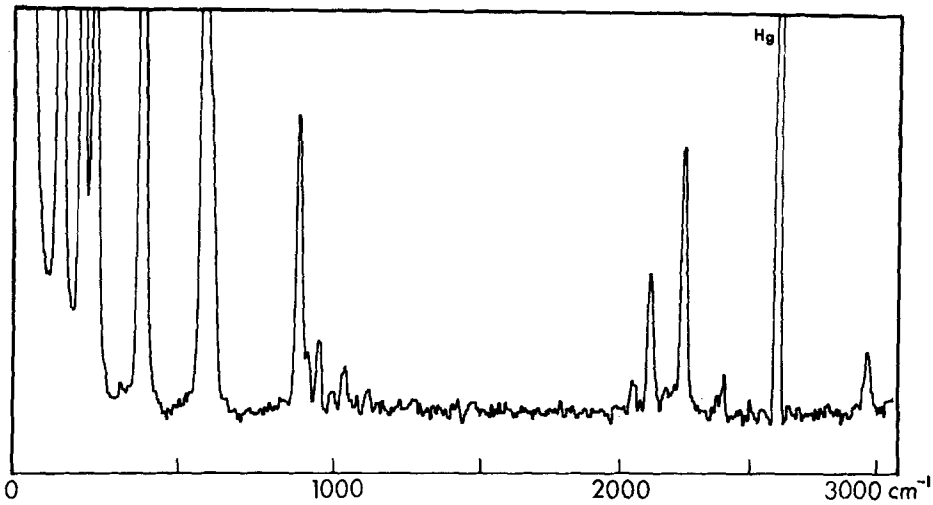

FIG. 4. Raman spectrum of liquid CD_3CBr_3 at 40°C

of the apparent absence of ν_{11} as being due to an accidental degeneracy with ν_5 not only agrees with the polarization results but also appears entirely consistent with the frequency pattern of the other two haloethanes (Fig. 5). The experimental results shown in Tables I and II agree well with literature values.

1,1,1-Tribromoethane. As was mentioned previously, this compound is so little known that many of its common physical properties are not listed in the

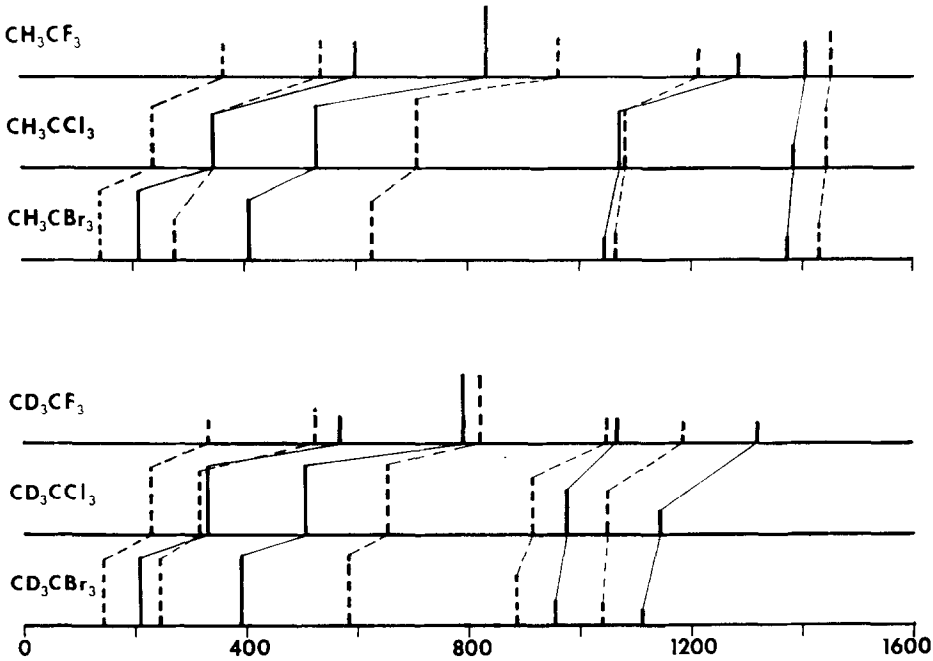

FIG. 5. Correlation diagrams for 1,1,1-trihaloethanes

literature. Few compounds containing a CBr_3 group have been studied spectroscopically. The experimental values of the fundamentals for the two isotopic species are also given in Tables I and II and tracings of the spectra are shown in Figs. 3 and 4.

Assignments for the bromo compound followed in a straightforward fashion from those made for the fluoro and chloro compounds. In the case of CH_3CBr_3, four medium to strongly polarized lines were observed which could readily be assigned to four of the A_1 species. The fifth, the symmetric CH_3 deformation ν_2, was assigned to the band at 1373 cm^{-1} although it was sufficiently low in intensity that its polarization state could not be determined reliably. However, the assignment is consistent with those for other members of the series. The assignment of ν_2 for the deuterated species was difficult since several lines clustered in the region around 1000 cm^{-1}. Since most of these were weak, polarization results were not definitive. The most intense maximum at 1083 cm^{-1} appeared to be depolarized and consequently is assigned as the E class deformation mode, ν_8. Of the remaining two maxima, the one at 1002 cm^{-1} can be assigned to a combination band (142 + 883 = 1025) leaving the band at 1110 cm^{-1} for the symmetric CD_3 deformation, ν_2. Although this assignment inverts the positions of ν_2 and ν_8 upon deuterium substitution, this is not disturbing since it also occurs

TABLE III

TELLER-REDLICH PRODUCT RULE RATIOS FOR METHYL HALOFORMS

	A_1 Class		E Class	
	Theor.	Exptl.	Theor.	Exptl.
CH_3CF_3/CD_3CF_3	1.963	1.921	2.615	2.536
CH_3CCl_3/CD_3CCl_3	1.976	1.979	2.696	2.629
CH_3CBr_3/CD_3CBr_3	1.987	1.999	2.756	2.752

in the chloride where the assignments are well established. The proposed assignments give good agreement with the theoretical Teller-Redlich product rule ratios calculated from the determinants of the inverse kinetic energy (G) matrices, as shown in Table III.

NORMAL COORDINATE CALCULATIONS

Normal coordinate calculations were performed on an IBM 7090 computer using an iterative least-squares procedure similar to that described by Overend and Scherer (*21*), Aldous and Mills (*22*), and others. Refinement was carried out in terms of symmetry force constants rather than on the basis of any more specialized force field. Data for both the hydrogen and deuterium species for a given halogen were fitted simultaneously and the deviation between observed and calculated frequencies were minimized using weighting factors proportional to the squared reciprocal frequency. Each symmetry class was treated separately. Since fewer frequencies were available than the number of force constants, it was necessary to constrain several constants. In general, the off-diagonal constants constrained either connected coordinates having no atoms in common, and therefore could be presumed to be quite small, or were found during the calculations to be relatively unimportant to the frequency fit. Only for the A_1 class of the fluoro and chloro compounds was the number of force constants calculated equal to the number of frequencies observed; in all other cases, fewer constants than frequencies were required.

The symmetry coordinates employed are given below. The numbering scheme for the atoms is straightforward and is identical with one described adequately in the literature (*23*) for a X_3YZW_3 molecule and consequently a sketch is not reproduced here. The symmetry coordinate, S_6, which belongs to the A_2 class has been omitted since the frequency is inactive. S_{01} and S_{02} are redundant coordinates involving the angles around the two carbon atoms.

Molecular Geometry for CH_3CX_3 :

$$r = \text{C–H}, \quad R = \text{C–C}, \quad d = \text{C–X},$$

$$\alpha = \text{H–C–H angle}, \quad \gamma = \text{X–C–X angle},$$

$$\beta = \text{H–C–C angle}, \quad \delta = \text{X–C–C angle}.$$

A_1 Symmetry coordinates:

$$S_{01} = 1/\sqrt{c_1}\,[\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3 + b_1(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)],$$
$$S_{02} = 1/\sqrt{c_3}\,[\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 + b_3(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)],$$
$$S_1 = 1/\sqrt{3}\,[\Delta r_1 + \Delta r_2 + \Delta r_3],$$
$$S_2 = 1/\sqrt{c_1}\,[b_1(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)],$$
$$S_3 = \Delta R,$$
$$S_4 = 1/\sqrt{3}\,[\Delta d_1 + \Delta d_2 + \Delta d_3],$$
$$S_5 = 1/\sqrt{c_3}\,[b_3(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3) - (\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)].$$

E Symmetry Coordinates:

$$S_7' = 1/\sqrt{2}\,[\Delta r_2 - \Delta r_3],$$
$$S_7'' = 1/\sqrt{6}\,[2\Delta r_1 - \Delta r_2 - \Delta r_3],$$
$$S_8' = 1/\sqrt{2}\,[\Delta\alpha_2 - \Delta\alpha_3],$$
$$S_8'' = 1/\sqrt{6}\,[2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3],$$
$$S_9' = 1/\sqrt{2}\,[\Delta\beta_2 - \Delta\beta_3],$$
$$S_9'' = 1/\sqrt{6}\,[2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3],$$
$$S_{10}' = 1/\sqrt{2}\,[\Delta d_2 - \Delta d_3],$$
$$S_{10}'' = 1/\sqrt{6}\,[2\Delta d_1 - \Delta d_2 - \Delta d_3],$$
$$S_{11}' = 1/\sqrt{2}\,[\Delta\gamma_2 - \Delta\gamma_3],$$
$$S_{11}'' = 1/\sqrt{6}\,[2\Delta\gamma_1 - \Delta\gamma_2 - \Delta\gamma_3],$$
$$S_{12}' = 1/\sqrt{2}\,[\Delta\delta_2 - \Delta\delta_3],$$
$$S_{12}'' = 1/\sqrt{6}\,[2\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3],$$

$$b_1 = -\sqrt{3}\cos\beta/\cos(\alpha/2), \qquad b_3 = -\sqrt{3}\cos\delta/\cos(\gamma/2),$$
$$c_1 = 3(b_1^2 + 1), \qquad c_3 = 3(b_3^2 + 1).$$

Values of the molecular parameters used in the calculations are given in Table IV. In the case of CH_3CBr_3 where no data were available, estimates were made from data on related compounds.

Elements of the inverse kinetic energy matrix were evaluated from the expressions given by Decius (*24*) and transformed into the symmetry coordinate basis by computer. Symmetry force constants obtained for all three molecules are listed in Table V while valence force stretching constants, which can be obtained from the symmetry constants without ambiguity, are given in Table VI.

TABLE IV

MOLECULAR PARAMETERS FOR CH_3CX_3 MOLECULES USED IN NORMAL COORDINATE ANALYSIS

Parameter	CH_3CF_3[a]	CH_3CCl_3[b]	CH_3CBr_3[c]
C–C dist. (Å)	1.512	1.550	1.540
C–X dist. (Å)	1.344	1.767	1.940
C–H dist. (Å)	1.093	1.093	1.093
XCX angle (°)	107.3	110.0	109.5
HCH angle (°)	109.5	109.5	109.5

[a] Ref. (*19*).
[b] Ref. (*20*).
[c] Estimated from other data.

TABLE V

SYMMETRY FORCE CONSTANTS FOR METHYL HALOFORMS

	CH_3CF_3	CH_3CCl_3	CH_3CBr_3		CH_3CF_3	CH_3CCl_3	CH_3CBr_3
A_1 Species				E Species			
$F_{1,1}$	4.899	4.929	4.965	$F_{7,7}$	4.896	4.770	4.750
$F_{2,2}$	0.616	0.580	0.590	$F_{8,8}$	0.539	0.538	0.525
$F_{3,3}$	4.251	3.171	3.163	$F_{9,9}$	0.557	0.649	0.590
$F_{4,4}$	7.328	4.715	3.269	$F_{10,10}$	4.571	2.366	2.820
$F_{5,5}$	2.005	1.369	1.529	$F_{11,11}$	1.841	1.441	1.094
				$F_{12,12}$	1.743	1.222	1.318
$F_{1,2}$	−0.389	−0.173	−0.037	$F_{7,8}$	0.030	0.111	0.025
$F_{1,3}$	0.0	0.0	0.0	$F_{7,9}$	0.0	0.0	0.0
$F_{1,4}$	0.0	0.0	0.0	$F_{7,10}$	0.0	0.0	0.0
$F_{1,5}$	0.0	0.0	0.0	$F_{7,11}$	0.0	0.0	0.0
$F_{2,3}$	−0.195	−0.212	−0.402	$F_{7,12}$	0.0	0.0	0.0
$F_{2,4}$	−0.231	−0.169	−0.497	$F_{8,9}$	0.0	0.0	0.0
$F_{2,5}$	0.0	0.0	0.0	$F_{8,10}$	0.0	0.0	0.0
$F_{3,4}$	1.184	−0.054	0.163	$F_{8,11}$	0.0	0.0	0.0
$F_{3,5}$	−0.533	−0.222	0.0	$F_{8,12}$	0.0	0.0	0.0
$F_{4,5}$	0.0	0.0	0.0	$F_{9,10}$	0.0	0.0	0.0
				$F_{9,11}$	0.0	0.0	0.0
				$F_{9,12}$	0.280	0.135	0.241
				$F_{10,11}$	0.306	0.0	0.0
				$F_{10,12}$	0.999	0.429	1.230
				$F_{11,12}$	0.918	0.657	0.137

Finally, the potential energy distributions among the symmetry coordinates are shown in Tables VII and VIII.

DISCUSSION

Of the three halides, the data for the fluoride were the most difficult to fit. The cause was not immediately apparent although it can be noted that the C–F

TABLE VI

VALENCE STRETCHING FORCE CONSTANTS FOR METHYL HALOFORMS (in md/Å)

Force constant	CH_3CF_3	CH_3CCl_3	CH_3CBr_3
f_r	4.897	4.823	4.822
f_d	5.490	3.149	2.970
f_R	4.251	3.171	3.163
f_{rr}	0.001	0.053	0.072
f_{dd}	0.919	0.783	0.150
f_{rd}	0.0	0.0	0.0
f'_{rd}	0.0	0.0	0.0
f_{rR}	0.0	0.0	0.0
f_{dR}	0.684	−0.031	0.094

stretching frequencies and the methyl group rocking and wagging motions occur in the same frequency region and extensive mixing results. The minimum in the hyper-surface explored by the least-squares calculations also appeared to be more shallow and the sides less steep than in the case of the other two halides. Other shallow minima corresponding to alternate force constant solutions were located but were not considered on physical grounds.

The classical motions of CH_3CF_3, as shown by the eigenvectors or potential energy matrices (Tables VII and VIII), agree generally with those given by Lafon and Nielsen (*6*) with the principal exception of the 1282-cm^{-1} frequency which is strongly mixed. Lafon and Nielsen found it to be dominated by the C–C stretch but in the present calculations, it consistently retained a major contribution from the CF_3 deformation despite its rather high frequency for this type of motion. The potential energy associated with the 827-cm^{-1} band, on the other hand, was about equally distributed between the C–F and C–C symmetry coordinates whereas Lafon and Nielsen regarded this band as due principally to C–F stretching. These differences serve to emphasize that the form of the normal coordinates is not independent of the nature of the force field used in the analysis, particularly in cases where the frequencies are mixed.

In the case of the other two haloethanes, descriptions of the normal coordinates are relatively straightforward, although mixing occurs in several of the frequencies. It is of some interest to note that the lowest E class frequency in these two cases is predominantly the CX_3 asymmetric deformation rather than the CX_3 rocking motion, as is the case in the fluoro compound.

The force constants in Tables V and VI show a few interesting features. In particular, all C–C stretching force constants have values significantly less than the value of 4.45 md/Å reported for ethane (*25*) also calculated on a symmetry coordinate basis. Structural data show that the C–C bond in the chloro compound is measurably (0.04 Å) longer than in the fluoro case. Although the uncertainty for the C–C distance in the chloro compound is larger than one would like, the difference appears real and is in agreement with the force constant trend.

TABLE VII

POTENTIAL ENERGY DISTRIBUTION IN SYMMETRY COORDINATE SPACE FOR A_1 CLASS FREQUENCIES OF METHYL HALOFORMS

CH_3CF_3	2970	1403	1282	827	600	CD_3CF_3	2170	1322	1065	798	568
S_1	0.96	0.04	0.00	0.00	0.00		0.92	0.02	0.07	0.00	0.00
S_2	0.04	0.73	0.21	0.01	0.02		0.06	0.03	0.75	0.07	0.09
S_3	0.00	0.11	0.14	0.48	0.27		0.02	0.26	0.05	0.32	0.35
S_4	0.00	0.07	0.25	0.51	0.16		0.00	0.30	0.05	0.55	0.09
S_5	0.00	0.05	0.40	0.01	0.55		0.00	0.39	0.08	0.06	0.47
CH_3CCl_3	2943	1384	1071	525	343	CD_3CCl_3	2130	1142	975	504	332
S_1	0.99	0.01	0.00	0.00	0.00		0.96	0.03	0.01	0.00	0.00
S_2	0.01	0.95	0.04	−0.01	0.00		0.03	0.35	0.60	0.01	0.01
S_3	0.00	0.03	0.53	0.40	0.04		0.01	0.40	0.13	0.40	0.06
S_4	0.00	0.01	0.23	0.54	0.22		0.00	0.14	0.12	0.57	0.17
S_5	0.00	0.00	0.20	0.06	0.74		0.00	0.08	0.14	0.02	0.75
CH_3CBr_3	2938	1373	1045	408	211	CD_3CBr_3	2116	1110	953	388	209
S_1	1.00	0.00	0.00	0.00	0.00		0.98	0.01	0.00	0.00	0.00
S_2	0.00	1.00	0.02	−0.03	0.01		0.01	0.41	0.60	−0.04	0.01
S_3	0.00	−0.01	0.66	0.35	0.00		0.01	0.36	0.26	0.37	0.01
S_4	0.00	0.01	0.09	0.31	0.58		0.00	0.11	−0.01	0.34	0.55
S_5	0.00	0.00	0.22	0.36	0.41		0.00	0.10	0.15	0.32	0.43

TABLE VIII

POTENTIAL ENERGY DISTRIBUTION IN SYMMETRY COORDINATE SPACE FOR E CLASS FREQUENCIES OF METHYL HALOFORMS

CH_3CF_3	3038	1452	1214	963	538	366	CD_3CF_3	2281	1182	1045	820	522	332
S_7	0.99	0.02	0.00	0.00	0.00	0.00		0.97	0.00	0.01	0.01	0.00	0.00
S_8	0.01	0.91	0.06	0.01	0.01	0.01		0.01	0.02	0.94	0.01	0.01	0.01
S_9	0.00	0.06	0.27	0.47	0.08	0.12		0.01	0.13	0.00	0.53	0.10	0.24
S_{10}	0.00	0.01	0.51	0.31	0.16	0.00		0.00	0.70	0.02	0.10	0.20	−0.02
S_{11}	0.00	0.00	0.11	0.12	0.51	0.25		0.00	0.18	0.00	0.08	0.61	0.14
S_{12}	0.00	0.00	0.04	0.08	0.24	0.63		0.01	−0.03	0.03	0.27	0.08	0.64
CH_3CCl_3	3009	1444	1079	711	343	238	CD_3CCl_3	2259	1050	914	654	316	231
S_7	0.99	0.01	0.01	0.00	0.00	0.00		0.97	0.02	0.01	0.00	0.00	0.00
S_8	0.01	0.91	0.07	0.00	0.01	0.00		0.02	0.91	0.05	0.00	0.01	0.00
S_9	0.00	0.08	0.76	0.10	0.04	0.01		0.01	0.06	0.52	0.31	0.07	0.03
S_{10}	0.00	0.00	0.07	0.79	0.00	0.14		0.00	0.01	0.27	0.59	0.03	0.11
S_{11}	0.00	0.00	0.00	0.17	0.19	0.63		0.00	0.00	0.03	0.15	0.32	0.50
S_{12}	0.00	0.00	0.09	−0.06	0.76	0.22		0.00	0.00	0.12	−0.05	0.57	0.36
CH_3CBr_3	2993	1432	1064	628	275	145	CD_3CBr_3	2241	1038	883	583	244	142
S_7	0.99	0.00	0.00	0.00	0.00	0.00		0.97	0.01	0.01	0.00	0.00	0.00
S_8	0.01	0.93	0.06	0.00	0.01	0.00		0.01	0.95	0.03	0.00	0.01	0.00
S_9	0.00	0.06	0.78	0.06	0.09	0.00		0.01	0.03	0.64	0.17	0.14	0.01
S_{10}	0.00	0.00	0.03	0.92	−0.15	0.20		0.00	0.01	0.13	0.81	−0.14	0.19
S_{11}	0.00	0.00	0.01	0.19	0.05	0.74		0.00	0.00	0.04	0.15	0.09	0.71
S_{12}	0.00	0.00	0.11	−0.17	1.00	0.05		0.01	0.00	0.14	−0.13	0.90	0.08

More accurate data for the chloro compound, and data for the bromo compound, would be of considerable interest for comparison with the results of the present calculations. Despite its higher force constant, the C–C distance in ethane (1.534 Å) is significantly longer than in 1,1,1-trifluoroethane. Clearly, these differences would seem to merit further attention with respect to the electron distributions involved and the particular differences in the halogens.

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