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THE VIBRATIONAL SPECTRA OF 1-CHLORO-1-HYDRO-F-ETHANE, $CF_3CHFC\ell$,
AND 1-BROMO-1-HYDRO-F-ETHANE, CF_3CHFBr

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SUMMARY

Infrared and Raman spectra were obtained for the fluorinated ethanes, $CF_3CHFC\ell$ and CF_3CHFBr , and their deuterated isotopomers. A vibrational assignment of these molecules is reported.

INTRODUCTION

Over the past two decades, there has been substantial interest in the vibrational properties of fluorocarbons and polyfluorinated hydrocarbons [1,2]. However, not very many vibrational studies have been concerned with the members of these classes which possess low symmetry. Recently there has been much activity in the area of vibrational spectroscopy of chiral molecules particularly with respect to the observation of vibrational optical activity by circular differential Raman scattering [3,4]. These studies can be furthered by first obtaining knowledge of the normal modes of vibration for the simpler chiral fluorocarbon molecules [5].

In addition, the fluorinated ethanes, $CF_3CHC\ell F$ and CF_3CHBrF , are related to the widely used anesthetic $CF_3CHC\ell Br$ (Halothane) [6]. In fact, CF_3CHBrF (Teflurane) has also been used as an anesthetic although its use has not been approved in the United States. Long path length infrared spectroscopy has been suggested as a means of monitoring the levels of anesthetics in operating rooms in order to ensure

the safety of personnel spending considerable time in this environment [6]. For these reasons, we undertook a vibrational study of the 1-halo-1-hydro-F-ethanes, CF_3CHClF and CF_3CHBrF . In this paper, we report a vibrational assignment of these substances and their deuterated derivatives.

EXPERIMENTAL

1-Chloro-1-hydro-F-ethane was prepared by the method of Miller, et al. [7]. This procedure involves addition of the elements of HF across the double bond of $\text{CF}_2=\text{CFC}\ell$ using a mixture of KF and formamide. The mixture was held between 30° and 40°C with stirring for nine days. The volatile product was removed and purified by fractional condensation and glpc (Column I: 11' x 1/4", 20% FS-1265 on a/w chromosorb W; Column II: 11' x 1/4", 15% dodecylphthalate on chromosorb P). The infrared spectrum matched that reported by Goldwhite et al. [8] CF_3CHClF . M: Calcd., 136 g/gmv. Found, 136 g/gmv.

1-Bromo-1-hydro-F-ethane was prepared in a manner similar to that described by Seyferth et al. using $\text{CF}_2=\text{CFBr}$ [9]. The reaction mixture was stirred at 50°C for seven days after which the volatile product was removed and purified by fractional condensation and glpc (Column II). The infrared spectrum agreed with that reported by Sharp and Coyle [10]. CF_3CHBrF . M: Calcd., 181 g/gmv. Found, 181 g/gmv.

The olefins, $\text{CF}_2=\text{CFC}\ell$ and $\text{CF}_2=\text{CFBr}$, were purchased from PCR, Inc. Purity was checked by vapor density measurements and infrared spectroscopy [11,12].

Formamide was purchased from Eastman Chemicals and purified by vacuum distillation. The fraction boiling at $50-50.5^\circ$ (0.5 mm Hg) was collected.

Potassium fluoride was purchased from Baker and Adamson and thermally dehydrated prior to use.

The deuterated derivative, $\text{CF}_3\text{CDC}\ell\text{F}$, was prepared by the exchange of hydrogen in CF_3CHClF (0.0991 g) with deuterium in a large excess of CH_3OD (33:1) to which a small amount of sodium (0.0020 g) had been added to generate NaOCH_3 . The reaction mixture was stirred at room temperature for 2 days and fractionated. The ratio of the normalized intensities of the C-D and C-H stretching vibrations in the Raman spectrum was about 4 to 1 indicating that roughly 80% exchange had

been accomplished. The partially exchanged material was stirred for 10 days with a fresh $\text{CH}_3\text{OD}/\text{NaOCH}_3$ mixture as before, and the product was purified by repeated fractional condensation. The Raman spectrum of this material showed a very small feature in the C-H stretching region indicating that almost complete exchange had occurred. $\text{CF}_3\text{CDC}^2\text{F}$: Recovered 0.0873 g, 87%. M: Calcd., 137 g/gmv. Found, 136 g/gmv.

Prior to using the method described above, exchange was attempted by stirring CF_3CHClF with a large excess of D_2O containing a small amount of NaOD for 5 days at room temperature. The procedure was repeated for 5 additional days with a fresh $\text{D}_2\text{O}/\text{NaOD}$ mixture. After this time, Raman evidence indicated that only about 50% exchange had occurred and some olefin (infrared band at 1800 cm^{-1}) was present. This method was abandoned in favor of the reaction involving CH_3OD .

CF_3CDBrF was prepared by stirring for 6 days a mixture of CF_3CHBrF (0.2167 g) and a large excess of D_2O (20:1) in which a catalytic amount of NaOD had been generated by the addition of Na (0.0024 g). The product was then added to a fresh $\text{D}_2\text{O}/\text{NaOD}$ mixture and stirred as before for 10 days. Recovered: 0.1841 g., 70%. CF_3CDBrF . M: Calcd., 182 g/gmv. Found, 183 g/gmv.

Infrared spectra were recorded on a P/E model 621 spectrophotometer using a 10 cm cell with KBr or CsI windows. The instrument was purged with dry CO_2 -free air. Spectra from which PR separations in the gas phase were measured were recorded using a Digilab Model FTS-10 Fourier Transform Infrared Spectrophotometer operating over the region $4000\text{-}450\text{ cm}^{-1}$ at a resolution of 0.5 cm^{-1} (KBr, 10 cm cell). Liquid phase Raman spectra were recorded on a Beckman Model 700 Raman spectrometer equipped with a Spectra-Physics 2-W argon-ion laser. Samples were held in capillaries and spectra were taken at two different wavelengths (4800 \AA and 5145 \AA) to detect any spurious peaks arising from imperfections in the grating. Gas phase Raman spectra were taken using a Spex Ramalog (CR-10 laser) or Cary 82 (5-W argon-ion laser) Raman spectrometer at a resolution of 2 cm^{-1} . A multi-pass system reflected the laser light through the sample held in a 5 cm cell equipped with quartz windows sealed to the cell at an angle of 45° . The emission lines of neon were used to calibrate the instruments, and spectral grade CCl_4 was employed to determine the resolution.

Infrared and Raman data for CF_3CHClF and CF_3CHBrF and their deuterated derivatives are presented in Tables I and II.

TABLE I

Vibrational Data For CF_3CDClF and CF_3CDBrF

CF_3CDClF						CF_3CDBrF						Assignment		
Raman		Infrared				Raman		Infrared						
gas		liquid		gas	gas	liquid		gas		gas				
ν	I	ν	I	ρ	ν	I	ν	I	ρ	ν	I			
3002	100	2998	23	0.16	3002	w	3007	100	3002	18	0.15	3007	w	C-H stretching, ν_1
					2196	vw						2194	mw	$2\nu_7$
					1670	vw								$\nu_3 + \nu_{14}, \nu_7 + \nu_{11}$
					1454	vw						1435	vw	$\nu_5 + \nu_{16}, \nu_8 + \nu_{11}$
1378	2	1373	4	0.52	1378	s	1370	1	1365	3	0.31	1369	s	C-C stretching, ν_2
1299	4	1290	7	0.71	1299	s	1290	<1	1281	2	0.32	1289	s	CF_3 stretching, ν_3
1287	2				1286	vs	1261	11	1254	10	0.17	1260	ms	C-H bending, ν_4
1212	2	1205	2	0.67	1212	vs	1209	<1	1201	2	0.33	1209	vvs	CF_3 stretching, ν_5
1168	2	1165	4	0.76	1166	vvs	1160	2	1143	2	0.38	1152	vvs	C-H bending, ν_6
1105	3	1102	4	0.53	1107	vs	1104	1	1097	2	0.41	1103	vs	C-F stretching, ν_7
												1055	vw	$\nu_9 + \nu_{15}, \nu_9 + \nu_{14}$
					966	vw, bd								$\nu_5 - \nu_{16}$
886	2	890	7	0.46	887	vs	865	4	862	7	0.19	865	s	CF_3 stretching, ν_8
												795	w	$\nu_{11} + \nu_{16}$
819	94	823	100	0.08	819	ms	755	44	755	73	0.14	758	ms	C-X stretching, ν_9
					741	vw, bd								$2\nu_{14}$
698	26	700	29	0.18	697	s	691	13	688	17	0.20	691	s	CF_3 deformation, ν_{10}
685	2			0.25										$\nu_{13} + \nu_{16}$
568	2	580	8	0.62	573	w	570	1	568	3	0.65	570	w	CF_3 deformation, ν_{11}
532	10	540	21	0.20	532	w	524	6	524	12	0.21	524	w	CF_3 deformation, ν_{12}
					512	vw	498	<1				494	vw	$\nu_{13} + \nu_{18}$
					498	vw						477	vw	$\nu_9 - \nu_{15}$
					481	vw								$2\nu_{16}$
451	28	456	53	0.11			428	18	429	27	0.15			CCF bending, ν_{13}
378	14	383	45	0.29			310	48	311	100	0.24			CFX scissors, ν_{14}
321	12	335	30	0.38			(300)							CF_3 rocking, ν_{15}
241	3	247	7	0.52			236	2	240	5	0.28			CF_3 rocking, ν_{16}
189	5	197	15	0.24			157	8	162	13	0.32			CCX bending, ν_{17}
70	3						67	4						CF_3 torsion, ν_{18}

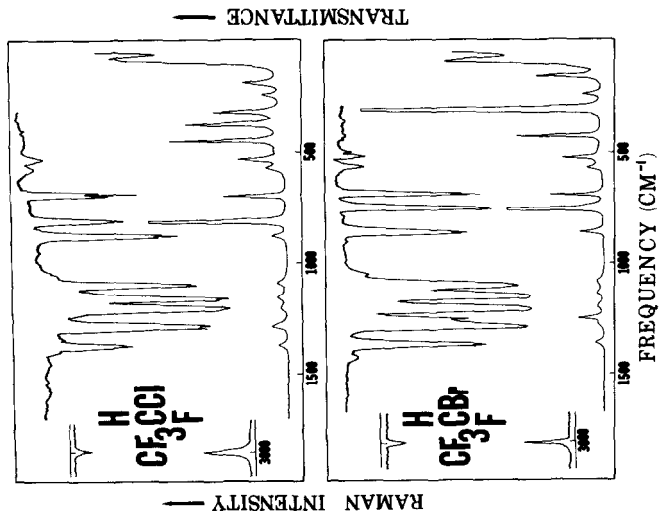


Fig. 1. Infrared and Raman spectra of CF_3CHClF and CF_3CHBrF .

CF_3CHClF : Infrared; gas phase, pressure 10 mm; gain, 5; suppress, 6; slit program, 1000; atten. speed, 1100; scan time, 36 min. Raman; liquid cap.; sens, 50; slits, 8/8/8; height, 12; time const, auto; scan speed 50 $\text{cm}^{-1}/\text{min}$, laser power at 488.0 nm, 400 mW.

CF_3CHBrF : Infrared; same as above. Raman; same as above except: sens, 24; laser power at 488.0 nm, 20 mW.

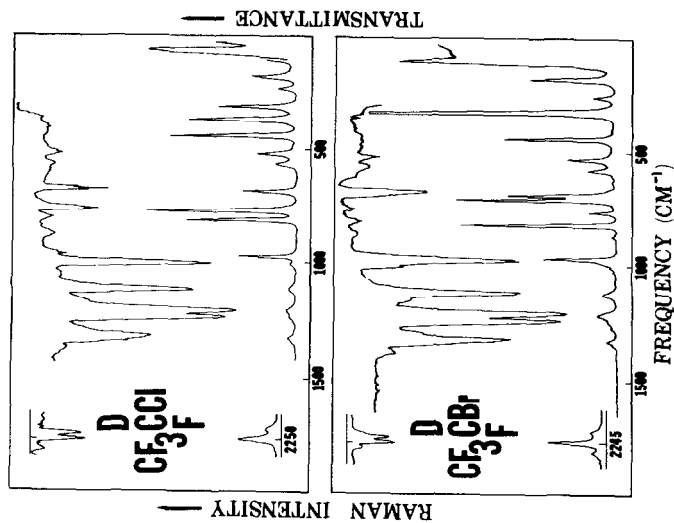


Fig. 2. Infrared and Raman spectra of CF_3CDClF and CF_3CDBrF .

CF_3CDClF : Infrared; same parameters as for CF_3CHClF except: pressure, 7 mm (50 mm for scan over 2250 cm^{-1}) Raman; same parameters as for CF_3CHClF except: sens, 90; laser power at 488.0 nm, 200 mW.

CF_3CDBrF : Infrared, same as above; Raman, same as for CF_3CHClF except: sens, 60; scan speed, 100 $\text{cm}^{-1}/\text{min}$.; laser power at 488.0 nm, 150 mW.

TABLE II

Vibrational Data For CF_3CDClF and CF_3CDBrF

CF_3CDClF						CF_3CDBrF						Assignment		
Raman		Infrared				Raman		Infrared						
gas	liquid	gas	gas	gas	gas	gas	liquid	gas	gas	gas				
ν	I	ν	I	ρ	ν	I	ν	I	ν	I	ρ	ν	I	
3010	2	3000	<1				3000	1	3000	1				*
2840	4											2360	vw	$\nu_3+\nu_7$
							2329	<1						$\nu_5+\nu_7$
		2325	3				2312	1			2303	vw		$\nu_2+\nu_4$
		2286	3	0.33			2298	2	2289	4	0.23			$\nu_2+\nu_6$
2258	29	2248	33	0.20	2257	w	2251	13	2246	16	0.27	2252	w	C-D stretching, ν_1
2251	22						2221	<1				2226	w,sh	$\nu_3+\nu_4$
2222	17													$\nu_4+\nu_5$
2212	20	2206	10	0.33	2211	w	2211	4	2202	7	0.35	2215	w	$\nu_3+\nu_6$
							2072	1	2065	<1				$\nu_6+\nu_7$
		2067	1											$\nu_2+\nu_9$
					2051	vw						2047	vw	$\nu_3+\nu_8$
					1375	vw	1372	<1	1372	<1		1370	vw	*
		1341	4	0.38	1343	w,sh	1332	<1	1331	<1		1333	w,sh	$2\nu_{10}$
1330	3	1321	7	0.34	1323	m	1319	2	1316	2	0.41	1320	s	C-C stretching, ν_2
					1296	vw						1289	vw	*
							1259	2	1255	1				$\nu_9+\nu_{11}$
		1252	2	0.48										$\nu_{10}+\nu_{11}$
1240	3	1234	6	0.52	1243	vs	1240	2	1230	3	0.52	1241	vs	CF_3 stretching, ν_3
1220	5	1204	8	0.40	1206	vvs	1207	5	1196	5	0.37	1212	vvs	CF_3 stretching, ν_5
					1167	w						1150	vw	*
1125	4	1113	6	0.51	1125	vs	1119	4	1109	5	0.53	1123	vvs	CF stretching, ν_7
1125	4	1113	6	0.51	1125	vs	1119	4	1109	5	0.53	1123	vvs	CF stretching, ν_7
							1045	4	1051	<1				$\nu_4+\nu_{18}$
					1034	vw								$\nu_{10}+\nu_{14}$
							1006	<1	1003	2	0.32	1005	vw	$\nu_9+\nu_{14}$
							998	<1						$\nu_9+\nu_{15}$
1012	8	1001	5	0.46	1009	vs	986	vw	985	<1		980	vs	C-D bending, ν_4
972	39	972	34	0.13	972	vw	961	16	962	15	0.21	961	w,sh	C-D bending, ν_6
					885	vw			862	<1		866	vw	*

TABLE II (cont.)

CF ₃ CDClF					CF ₃ CDBrF							Assignment		
Raman					Infrared		Raman						Infrared	
gas		liquid			gas		gas		liquid				gas	
ν	I	ν	I	ρ	ν	I	ν	I	ν	I	ρ		ν	I
815	70	812	70	0.11	812	w	810	30	809	26	0.14	811	vw	CF ₃ stretching, ν ₈
							755	<1	755	<1				*
775	100	772	100	0.13	774	m	695	36	697	32	0.21	691	m	CX stretching, ν ₉
687	31	685	35	0.18	685	s	677	25	679	21	0.23	677	m	CF ₃ deformation, ν ₁₀
							653	2	650	2	0.28			ν ₁₃ ⁺ ν ₁₆
					612	vw								ν ₁₂ ⁺ ν ₁₈ , ν ₁₄ ⁺ ν ₁₆
582	1						585	<1						
569	2	568	13	0.64	572	vw	565	5	562	7		566	vw	CF ₃ deformation, ν ₁₁
526	12	520	25	0.18	523	vw	517	10	516	8	0.25	517	vw	CF ₃ deformation, ν ₁₂
		490	2											2ν ₁₆
							473	vw				481	vw	ν ₁₃ ⁺ ν ₁₈
														ν ₁₄ ⁺ ν ₁₈
449	45	449	81	0.13			424	32	425	18	0.20			CCF bending, ν ₁₃
378	27	378	70	0.26			308	100	309	100	0.23			CFX scissors, ν ₁₄
324	26	323	50	0.30			(300)							CF ₃ rocking, ν ₁₅
246	sh													
240	6	245	11	0.27			235	5	238	4	0.38			CF ₃ rocking, ν ₁₆
194	9	195	27	0.38			156	20	160	4	0.33			CCX bending, ν ₁₇
80	17						67	12						CF ₃ torsion, ν ₁₈
66	12													

*Indicates CF₃CHF impurity.

DISCUSSION

The compounds, CH₃CHClF and CF₃CHBrF, belong to the point group C₁, and therefore, the expected eighteen normal modes of vibration are all singly degenerate of species a. All eighteen fundamentals were observed in both the gas and liquid phases; the only differences were a general lowering of the frequencies in the liquid and changes in the intensities of some of the bands. Since symmetry considerations are not particularly useful in assigning the fundamental transitions reported here, we have relied heavily on predicted frequency shifts, the Teller-Redlich Product rule and correlations with assigned frequencies of similar molecules. In particular Theimer and Neilsen

【13】 have interpreted the vibrational spectrum of CF_3CHBrCl , and Hudgens *et al.* 【5】 have reported the results of a study on CH_3CBrClF . Durig *et al.* 【14】 have investigated CH_3CHClF , and Crowder 【15】 has studied the series of compounds $\text{CF}_3\text{CH}_2\text{X}$ where $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$. Our description of the molecular motions is similar to that of Durig *et al.* (14) for CH_3CHClF , but it should be recognized that extensive mixing of the vibrational modes probably occurs and the representation of the motions given here is, at best, an approximation. A normal coordinate analysis of the $\text{CF}_3\text{CH}_2\text{X}$ series 【15】 indicated that the modes are highly mixed in those compounds.

CF_3 Vibrations Nine motions involving primarily the CF_3 group are expected. In C_{3v} symmetry these modes would be classified as the doubly degenerate antisymmetric and singly degenerate symmetric CF_3 stretching modes, the doubly degenerate antisymmetric and singly degenerate symmetric CF_3 deformations, two CF_3 rocking motions, and a CF_3 torsion. In C_1 symmetry the degenerate modes are split and all nine bands are observed.

Crowder 【15】 has argued that the symmetric CF_3 stretching mode is strongly mixed with the C-C stretch in $\text{CF}_3\text{CH}_2\text{X}$, with the lower frequency band having the greater contribution from the CF_3 moiety.

Accordingly, we assign a strong CF_3CHClF infrared band at 1378 cm^{-1} to the C-C stretching motion (1369 cm^{-1} in the bromo compound) and one at 887 cm^{-1} to the CF_3 symmetric stretch (865 cm^{-1} , bromo). These bands exhibit a rather unexpected frequency shift to 1323 and 812 cm^{-1} for CF_3CDClF (1320 and 811 , deuterio-bromo). This behavior is indicative of a substantial mixing of each of these vibrational modes with a C-H vibrational mode.

The two antisymmetric CF_3 stretching modes are well separated and appear as strong infrared bands at 1299 and 1212 cm^{-1} in CF_3CHClF (1289 and 1209 cm^{-1} , bromo). In the deuterated derivatives, they are shifted to 1243 and 1206 cm^{-1} (1241 and 1212 cm^{-1} , deuterio-bromo).

The symmetric CF_3 deformation usually appears in the $700\text{-}600 \text{ cm}^{-1}$ region as a strong feature in both the infrared and Raman spectra. It is observed at 697 cm^{-1} in CF_3CHClF (691 cm^{-1} , bromo) and 685 cm^{-1} in CF_3CDClF (677 cm^{-1} , deuterio-bromo). The usually less intense antisymmetric CF_3 deformations are observed at 573 and 532 cm^{-1} for CF_3CHClF (570 and 524 , bromo) and at 572 and 523 cm^{-1} for the deuterated derivative (566 and 517 , deuterio-bromo).

The CF_3 rocking modes are more difficult to assign but should appear at relatively low frequencies. Crowder [15] has placed the CF_3 rocks for CF_3CH_2Cl at 330 (a') and 355 (a''), but Lopata and Durig [16] have not observed a band at 330 cm^{-1} . They place the a' rock at 356.7 cm^{-1} . Theimer and Neilsen [13] have assigned the CF_3 rocking modes of $CF_3CHClBr$ to bands at 229 and 202 cm^{-1} . We observe features at 321 and 241 cm^{-1} for CF_3CHClF which probably have a large CF_3 rocking contribution. In the case of CF_3CHBrF , the intense $CFBr$ scissors mode probably obscures the higher frequency CF_3 rocking mode which is placed close to 300 cm^{-1} on the basis of the observation of certain combination bands. The lower frequency CF_3 rocking mode appears at 236 cm^{-1} . The corresponding modes for CF_3CHClF are observed at 324 and 240 cm^{-1} while the higher frequency rock for CF_3CDBrF is again obscured by the intense $CFBr$ scissors motion. The occurrence of several combination bands are again consistent with this assignment. The lower frequency rocking mode appears at 235 cm^{-1} .

The CF_3 torsions in molecules of this type should, on the basis of evidence reported in the literature be observed near or below 100 cm^{-1} . Lopata and Durig [16] found the torsional vibrations of CF_3CH_2Cl and CF_3CH_2Br at 93 and 89 cm^{-1} in a gas phase Raman study of these compounds. The only bands appearing in this region for CF_3CHClF and CF_3CHBrF are at 70 and 67 cm^{-1} ; we assign these to the torsions. The deuterated derivatives show similarly broad bands at 80 and 67 cm^{-1} . The upward shift again indicates mode mixing.

CHFX Vibrations and skeletal motions The CC stretching motion was treated above. The CH stretching mode appears as a very strong Raman emission at 3002 cm^{-1} and a weak infrared absorption at the same frequency (3007, bromo). These intensities are typical of CH stretching vibrations in fluorinated aliphatic compounds, [1] and they are shifted to 2257 and 2252 cm^{-1} in the deuterated derivatives ($\nu_1/\nu = 0.749, 0.748$).

The CF stretching mode is assigned at 1107 cm^{-1} for CF_3CHClF (1103, bromo) and is shifted significantly to a higher frequency upon deuterium substitution (1125 cm^{-1} , chloro; 1123 cm^{-1} , bromo). This is consistent with our assumption that the vibrational modes for these compounds are highly mixed since a general decrease in the vibrational frequencies is expected upon substitution.

The CCl and CBr stretching motions in CF_3CHClF and CF_3CHBrF are, as expected, quite strong in the Raman spectrum and moderately strong in the infrared spectrum at 819 and 758 cm^{-1} .

The CH bending modes are usually found in the 1350 to 1100 cm^{-1} region [3,13,14]. We observe them at 1286 and 1166 cm^{-1} for CF_3CHClF (1260 and 1152 cm^{-1} , bromo). Upon deuteration these modes shift to 1009 and 972 cm^{-1} for CF_3CDClF (980 and 961 cm^{-1} , deuterio-bromo). The isotopic shift ratios, 0.785 and 0.834 for the chloro derivative and 0.778 and 0.834 for the bromo derivative, again indicate that there is extensive mixing of the vibrational modes in these compounds since ratios near 0.71 are normally expected for an unmixed vibrational frequency shift.

The CCF, CCCl, and CCBBr bending modes are expected to occur at low frequency. A moderately intense Raman band at 451 cm^{-1} for CF_3CHClF (428 cm^{-1} , bromo) is assigned to the higher energy CCF bend which is not shifted in the deuterated derivatives (449 cm^{-1} , deuterio-chloro; 424 cm^{-1} , deuterio-bromo). The CCCl and CCBBr bending modes involve relatively massive atoms and occur at 189 and 157 cm^{-1} (194 and 156 cm for the deuterated compounds). The CFCl and CFBr scissors motions are also expected to appear as relatively strong Raman emissions at low frequency due to the large changes in polarizability accompanying the motions of these heavy atoms. The strong bands at 378 cm^{-1} in the spectrum of CF_3CHClF and 310 cm^{-1} in that of CF_3CHBrF are assigned to this vibration.

Band contours The center of mass and the principal moments of inertia were calculated for CF_3CHBrF and CF_3CDBrF using bond lengths and angles for similar compounds for which reasonably accurate data were available. The structural parameters used for this calculation were: C-C, 155 pm; C-F, 133 pm; C-H, 109.3 pm; C-Br, 193 pm; FCCF dihedral angle, 120°; F-C-F angle, 108°; F-C-C angle, 110.7°. Table III lists the principal moments of inertia from which the rotational constants were calculated.

The value of κ , the asymmetry factor, indicates that the geometry of the molecules is close to that for a prolate top. From these data, the vapor phase band contours were calculated in order to determine PR branch separation [18,19]. These values are listed in Table IV. Values for those bands which were reasonably well-resolved are listed.

TABLE III

PRINCIPAL MOMENTS OF INERTIA ($\text{amu}\cdot\text{A}^2$) AND ROTATIONAL CONSTANTS (cm^{-1})

	I_A	I_B	I_C	A	B	C	κ
CF_3CHBrF	163.7	434.6	505.6	0.1030	0.0388	0.0333	-0.8436
CF_3CDBrF	166.9	437.2	506.2	0.1010	0.0386	0.0333	-0.8450

TABLE IV

CALCULATED AND OBSERVED PR BRANCH SEPARATION

A	CALCULATED	CF_3CHBrF (cm^{-1})		CF_3CDBrF (cm^{-1})	
	TYPE A	10.2		10.0	
	TYPE B	17.6		16.6	
	TYPE C	6.0		6.0	

B	<u>OBSERVED</u>	CF_3CHBrF		CF_3CDBrF	
Vibrational Description	Q-branch (cm^{-1})	PR (cm^{-1})	Vibrational Description	Q-branch (cm^{-1})	PR (cm^{-1})
CC	1369	12.0			
CH	1152	10.00	CD	980	8.0
CF	1103	14.0	CF	1123	16.0
CF	865	10.0			
CBr	758	6.0			
CF	691	8.6			

The observed PR separations support the assignment of the vibrational modes. Note that the band assigned to the lone CF stretch at 1103 cm^{-1} has a strong B component which is consistent with the orientation of CF_3CHBrF with respect to the b-axis along which a large component of the CF vector lies. The band at 3002 cm^{-1} has the appearance of a C-type envelope which fits well with the orientation of the largest component of the CH bond vector along the c-axis. The PR separations of the bands at 1369 and 865 cm^{-1} which have been assigned to C-C and CF_3 are close to the values expected for A-type bands, but the orientation of the molecules is such that the vectors describing these vibrations have higher components along b and c than along a; however, the combination of separations for B and C could yield values in the range of $10\text{-}12\text{ cm}^{-1}$ as observed. The band

TABLE V

Summary of fundamental vibrations*

Assignment	Approximate Description	FREQUENCY (cm^{-1})			
		CF_3CHClF	CF_3CDClF	CF_3CHBrF	CF_3CDBrF
1	C-H stretch	3002	2257	3007	2252
2	C-C stretch	1378	1323	1369	1320
3	C-F stretch	1299	1243	1289	1241
4	C-H stretch	1286	1009	1260	980
5	C-F stretch	1212	1206	1209	1212
6	C-H bend	1166	972	1152	961
7	C-F stretch	1107	1125	1103	1123
8	C-F stretch	887	812	865	811
9	C-X stretch	819	774	758	691
10	CF def.**	697	685	691	677
11	CF def.**	573	572	570	566
12	CF def.**	532	523	524	517
13	CCF bdnd	451	449	428	424
14	CFX scissors	378	378	310	308
15	CF rock	321	324	(300)	(300)
16	CF rock	241	240	236	235
17	CCX bend	189	194	157	156
18	CF torsion	70	80	67	67

*Infrared gas phase frequencies used where possible. Otherwise, Raman gas phase frequencies were used except as noted.

**deformation

at 758 cm^{-1} is clearly of the A-type; this is consistent with the assignment of CBr to this feature since the CBr bond vector has its largest component along the a-axis.

As a further check on the consistency of this assignment, the Teller-Redlich product rule was applied using the calculated principal moments of inertia for CF_3CHBrF and CF_3CDBrF . The agreement between the left hand side of the equation (ratio of product of frequency ratios, 0.370) and the right hand side (ratio of masses, moments of inertia, etc., 0.361) was within 2.4%. This result indicates that the assignment is internally consistent, though it is not necessarily unique. A summary of the fundamental vibrations appears in Table V.

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