

## Fluoroalcohols

### Part 17.<sup>1</sup> Infrared and Raman Spectra of the Perhalogenated *t*-Butyl Alcohols $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ and $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OD}$

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Infrared spectra of gaseous and liquid and Raman spectra of liquid  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$  and  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OD}$  have been studied. Raman spectra of solutions of the former alcohol in carbon tetrachloride and dimethyl sulphoxide and the IR spectrum in carbon tetrachloride are reported. A vibrational assignment is made. The liquid alcohols are only little associated. The multiplicity of the OH stretching band indicates that three conformers are present in appreciable amounts in the vapour and at least two conformers in the neat liquid and in solutions of the alcohols in  $\text{CCl}_4$ . Combination bands  $\nu\text{OH} \pm \tau\text{OH}$  relating to only one conformer occur in the vapour spectra.

In connection with a study of the IR and Raman spectra of perfluorinated *t*-butyl alcohol (PFTB),<sup>2</sup> we synthesized 2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propanol ( $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ , TCHFb). This alcohol is quite acidic; its  $\text{p}K_a$  is only 5.1 at 25°.<sup>3</sup> We have recorded the IR and Raman spectra of TCHFb and its deuterated analogue  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OD}$  (TCHFb-*d*), mainly because it is one of the few alcohols containing a trichloromethyl group that can be studied both as a vapour and as a liquid at room temperature. The results are reported below.

#### EXPERIMENTAL

TCHFb was synthesized according to Dear<sup>4</sup> by ultraviolet photochemical chlorination of 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol in a Hanovia 1-litre photochemical reactor equipped with a 100 W medium pressure mercury lamp. The progress of the chlorination was followed with the aid of a Varian 1520-1B gas chromatograph equipped with a dinonyl phthalate column and a hydrogen flame ionisation detector. The product was very hygroscopic and was dried first with sodium sulphate and then with a large

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quantity of molecular sieves (type 4A). The product boiled at 139–140° and melted at –2°. The chemical shift  $\delta$  of the hydroxyl proton in the NMR spectrum of the neat liquid at a temperature of 39° was 3.90 ppm relative to tetramethylsilane. The purity of the compound exceeded 95 % as deduced from the NMR spectrum and the gas chromatogram, the main impurity being 2-dichloromethyl-1,1,1,3,3,3-hexafluoro-2-propanol.

TCHF $B$ - $d$  was obtained by shaking TCHF $B$  several times with deuterium oxide, distilling and drying.

Dimethyl sulphoxide (DMSO) was purified by fractional crystallization, and carbon tetrachloride was dried with molecular sieves (type 4A).

The IR spectra were recorded with a Perkin-Elmer 621 spectrometer equipped with an air drying unit. The frequency scale of the spectrometer was calibrated with atmospheric moisture and carbon dioxide. The vapour spectra were measured after injecting liquid alcohol into an evacuated Perkin-Elmer variable temperature cell (KBr windows, path length 5 cm) or a 1 m path length cell with CsI windows. When the spectrum of a liquid was recorded, the liquid was between window plates or in a sealed cell FH-01K (RIIC). Some spectra of the compounds in  $\text{CCl}_4$  were recorded also with a Beckman DK-2A spectrophotometer.

The Raman spectra were measured with a Jarrell-Ash 25–305 spectrometer equipped with an Orlando Ar/Kr ion laser (model 400 MG) of 2 W total efficiency. The exciting line was the 488 nm line of argon; its intensity at the sample was about 200 mW. The spectra were taken using 90° excitation from above. A half-wave plate, analyser and scrambler were always in the light path; polarization measurements were made after turning the analyser 90°. A slit servo system kept the spectral slit width constant at about 2  $\text{cm}^{-1}$ , which permitted the evaluation of relative band intensities. A liquid multipass cell of 2.5 ml capacity was used. We found that by using a screen that allows scattered light only from the liquid and not from the glass of the cell to enter the entrance slit, one can get about 10  $\text{cm}^{-1}$  closer to the exciting line.

The reported positions of sharp IR and Raman bands are believed to be accurate to  $\pm 2 \text{ cm}^{-1}$ . The non-SI units used are 1 Å =  $10^{-10}$  m and 1 amu =  $1.660 \times 10^{-24}$  g.

## RESULTS AND DISCUSSION

A TCHF $B$  molecule has 39 fundamental vibrational modes, of which, assuming  $C_s$  symmetry as the  $\text{CCl}_3$ ,  $\text{CF}_3$ , and OH groups are relatively freely rotating, 22 are of species  $a'$  and 17 of species  $a''$ . A complete assignment would therefore be difficult and is not attempted here.

The principal axes and moments of inertia of TCHF $B$  and TCHF $B$ - $d$  were computed using the programme CART written by Schachtschneider.<sup>5</sup> The values of the structural parameters used were the same as in the case of PFTB with the additions that the carbon-chlorine bond length was taken as 1.76 Å and that the angles Cl–C–Cl and C–C–Cl were assumed tetrahedral. The isotopic masses were used (for chlorine, the mass of  $^{35}\text{Cl}$ ).

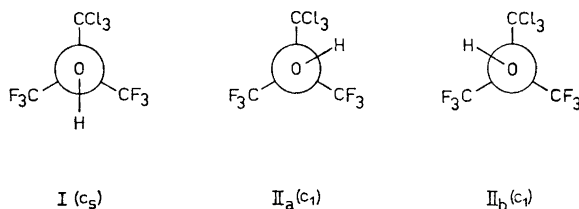


Fig. 1. Staggered conformers of TCHF $B$ . Conformers II $_a$  and II $_b$  are spectroscopically equivalent.

Table 1. IR and Raman spectra (values of  $\nu/\text{cm}^{-1}$ ) of  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$  (TCHF<sub>3</sub>B) and its solutions (excluding the region 1400–3200  $\text{cm}^{-1}$ ). Relative Raman intensities are given in parentheses (the intensity of the band at 410  $\text{cm}^{-1}$  = 100). P = polarized, DP = depolarized band; the figures after these are the depolarization ratios.  $\nu$  = stretching,  $\delta$  = bending,  $\rho$  = rocking, and  $\tau$  = torsion; sh = shoulder. Subscript s = symmetric, a = antisymmetric vibration.

Vapour IR	Liquid		Solution		Assignment
	IR	Raman	0.2 M in $\text{CCl}_4$ IR	37.7 wt. % in $\text{CCl}_4$ Raman	
3852 vvw	3835 vvw		3824 br, vw		3580 + 268
3625 vw	3667 vw		3580 sh		$\nu_s\text{OH}$ , conf.(i)
3603 m	3585 sh	P	3553 br, s	3560 P	$\nu_s\text{OH}$ , conf.(ii)
3580 w	3563 m	P (3)			$\nu_s\text{OH}$ , conf.(iii)
3304 vvw				1365 DP?	3580–268
1370 m	1363 m	P (1)	1364 w		$\delta_s\text{OH}$
1325 vw <sup>a</sup>	1335 sh <sup>a</sup>		1332 sh <sup>a</sup>		$\nu_a\text{CF}_3$
1269 vvs	1269 vvs	DP (2)	1265 vs	1270 DP	$\nu_s\text{CF}_3$
1243 vvs	1238 (3)	P (3)	1234 vvs	1238 P	$\nu_s\text{CF}_3$
1227 sh	1225 vvs	P (3)	1227 (3)	1228 P	$\nu_a\text{CF}_3$
1217 vvs	1212 (3)	P?	1212 vs	1213	
1165 w <sup>a</sup>	1195 sh?	DP?	1161 w <sup>a</sup>		$\nu_a\text{CF}_3$
1147 vs	1155 sh <sup>a</sup>	DP (0.8 <sup>a</sup> )	1142 vs	1153a	$\nu_s\text{CF}_3$
1100 sh	1136 vs	DP (<1)	1090 vvw		
1026 w	1022 w	P (3)	1023 w	1020 P	$\nu_s\text{skel.}$
956 w	952 m	DP (1)	953 w	952 DP	$\nu_a\text{skel.}$
850 m	842 m	DP (2)	846 m	846 DP	$\nu_s\text{CCl}_3$
790 m	787 m	P (6)	788 (6)	789 DP	$\nu_s\text{CCl}_3$
726 s	722 s	P (44)	724 (44)	724 P	$\nu_s\text{skel.}$
724 sh	708 s	DP?	709 s		$\delta_a\text{CF}_3$
711 s					

620 vvw	624 vvw	624 (5)	P	0.7	624 vvw	624 DP	624 DP	$\delta_s CF_3$
563 vvw	564 vvw	565 (1)	DP	0.8	564 vvw	567 DP	567 DP	$\delta_a CF_3$
540 w	548 w	542 (2)	DP	0.7	540 vw	541 DP	541 DP	$\delta_s CF_3, \rho_a CF_3$
490 vw	491 w	493 (19)	P	0.1	490 vw		~ 545	$\delta_s CF_3, \rho_a CF_3$
409 vvw	409 vvw	410 (100)	P	0.01	409 vvw		494 P	$\delta_s$ skel.
360 vvw	359 vvw	355 (7)	DP	0.7	360 vvw		410 P	$\nu_s CCl_3$
	328 vvw	328 (15)	P	< 0.1				$\delta_a$ skel.
295 vw	294 vw	317 (15)	DP	0.7				$\delta_s$ skel.
287 vvw		292 (24)	DP	0.8				$\rho_a CF_3$
268 w	273 vw	285 sh	DP				292 sh <sup>b</sup>	$\rho_a CCl_3, \delta_a CF_3$
	257 vw							
	217 vvw	256 (17)	P	0.4				$\tau_a OH$
		222 (16)	P	0.5			256 P	$\delta_s CCl_3$
209 vvw		209 (16)	P	0.7			225 P	$\rho_s CF_3$
		192 (3)	DP	0.8			210 DP	$\delta_s CCl_3$
		169 (6)	P	0.7			170	$\rho_s CCl_3, \rho_a CCl_3$
		70br (1)	DP	0.8?				$\rho_s CF_3, \tau CCl_3$

<sup>a</sup> The band may also be due to the dichloro compound. <sup>b</sup> Solvent bands may be present in this region. <sup>c</sup> The SO stretching band of pure DMSO is at 1045 cm<sup>-1</sup>. In spectra of its mixtures with TCHFB, the band is at 1050 cm<sup>-1</sup> and is slightly broader. Also the broad shoulder at 1020 cm<sup>-1</sup> may in part be due to SO stretching (cf. HFP<sup>18</sup> and PFTB<sup>2</sup>).

TCHFb should have only two different conformers with respect to rotation of the hydroxyl group around the C–O bond if we accept only conformers where the O–H bond is staggered with respect to the C–C bonds (conformers I and II in Fig. 1; the structures II<sub>a</sub> and II<sub>b</sub> are spectroscopically equiv-

Table 2. IR and Raman spectra of CCl<sub>3</sub>C(CF<sub>3</sub>)<sub>2</sub>OD (TCHFb-d). Above 1500 cm<sup>-1</sup>, only bands associated with OD stretching are given.

Vapour IR	IR	Liquid	Raman <sup>a</sup>		Assignment
2850 vvw	2830 vvw 2730 vvw				2644 + 205
2672 sh					$\nu_s$ OD, conf. (i)
2660 m	2632 m	2640	P	0.2	$\nu_s$ OD, conf. (ii)
2644 w		2610 sh?	P		$\nu_s$ OD, conf. (iii)
2440 vvw					2644 – 205
1367 vw <sup>b</sup>					
1318 sh	1318 sh				
1290 vs	1284 vs	1289 (2)	P	0.7	$\nu_s$ CF <sub>3</sub>
1267 vvs	1258 vvs	1262 (2)	DP	0.8	$\nu_a$ CF <sub>3</sub>
1243 vvs		1243	P?		$\nu_s$ CF <sub>3</sub>
	1228 vvs	1230 (2)			$\nu_a$ CF <sub>3</sub>
1218 sh <sup>b</sup>					
	1200 sh	1200 (<1)	DP		
1168 m	1163 sh	1162 (1)	P		$\nu_s$ CF <sub>3</sub>
1151 s	1150 s	1152 (1)	DP	0.8	$\nu_a$ CF <sub>3</sub>
		1110 (1)	P	<0.3	
1075 m	1070 m	1070 (1)	P	0.5	$\delta_s$ OD
1008 m	1007 m	1007 (2)	P	0.4	$\nu_s$ skel.
	973 vvw				
953 vw <sup>b</sup>	952 vvw <sup>b</sup>				
882 sh?					
878 m	877 m	878 (2)	DP?		$\nu_a$ skel.
845 m	838 m	837 (3)	DP	0.7	$\nu_a$ CCl <sub>3</sub>
793 m	789 m	789 (8)	P	0.5	$\nu_s$ CCl <sub>3</sub>
726 s	724 s	725 (32)	P	0.04	$\nu_s$ skel.
705 m	699 m	700 (2)	P		$\delta_a$ CF <sub>3</sub>
617 vvw	617 vw	619 (5)	P	0.5	$\delta_s$ CF <sub>3</sub>
	564 vvw	566 (1)	DP		$\delta_a$ CF <sub>3</sub>
537 w	539 w	542 (2)	P	0.6	$\delta_s$ CF <sub>3</sub> , $\delta_a$ CF <sub>3</sub>
487 w	487 w	489 (20)	P	0.1	$\delta_s$ skel.
		433 sh(1)	P	0.1	
	409 vvw	409 (100)	P	0.03	$\nu_s$ CCl <sub>3</sub>
		355 (6)	DP	0.8	$\delta_a$ skel.
		329 (16)	P	0.2	$\delta_s$ skel.
		319 (15)	DP	0.7	$\nu_a$ CF <sub>3</sub>
		292 (22)	DP	0.8	$\delta_a$ CCl <sub>3</sub> , $\nu_a$ CF <sub>3</sub>
		258 (13)	P	0.4	$\delta_s$ CCl <sub>3</sub>
		224 (16)	P	0.5	$\nu_s$ CF <sub>3</sub>
		210 (15)	DP	0.7	$\delta_s$ CCl <sub>3</sub>
		193 (2)	P	0.6	$\nu_s$ CCl <sub>3</sub> , $\nu_a$ CCl <sub>3</sub>
		170 (5)	DP?		$\nu_s$ CF <sub>3</sub>
		70 br	P?		$\tau$ CF <sub>3</sub> , $\tau$ CCl <sub>3</sub>

<sup>a</sup> The data in the region 1000–1400 cm<sup>-1</sup> are incomplete because of the low intensities of the bands. <sup>b</sup> This band may be due to the undeuterated compound.

alent). The principal moments of inertia vary very little from conformer to conformer. For structure I (denoted by (i) in the tables; see below) we obtained the values  $I_A = 789.7$  (794.6),  $I_B = 885.7$  (892.2), and  $I_C = 1111.3$  (1113.0) amu  $\text{\AA}^2$  (the values in parentheses are those obtained for the deuterated compound). The principal axes A and C are in the plane defined by the O-H, C-O and C- $\text{CCl}_3$  bonds and the C axis is almost parallel to the C-O bond and *ca.* 0.3  $\text{\AA}$  towards the  $\text{CCl}_3$  group. The A and B axes lie almost in the plane of the three carbon atoms of the trihalogenomethyl groups.

Band contours in the vapour spectra and moments of inertia give relatively little information because of the large moments of inertia and relatively high boiling points of the compounds. Only the band at  $490\text{ cm}^{-1}$  has a comparatively well-defined contour (Fig. 2B), which is similar to the "perpendicular" OH stretching band of PFTB.<sup>2</sup> Also the band at  $726\text{ cm}^{-1}$  seems to be somewhat similar in shape. The bands at  $852$ ,  $623$ , and  $360\text{ cm}^{-1}$  seem to be triangular.

*OH (OD) stretching.* Chloroalcohols usually show marked splitting of the OH stretching band due to conformational heterogeneity.<sup>6-8</sup> The OH stretching band in the vapour spectrum of TCHF<sub>3</sub> is a triplet with maxima at  $3625$ ,  $3603$ , and  $3580\text{ cm}^{-1}$  (Figs. 2 and 4). The value  $3625\text{ cm}^{-1}$  is about the same as that found for the  $C_s$  conformer of hexafluoro-2-propanol (HFP);<sup>9</sup> also gaseous hexafluoro-*t*-butyl alcohol (HFTB) has a band at this wavenumber.<sup>10</sup> We thus assign the band at  $3625\text{ cm}^{-1}$  to a symmetric conformer, type I in Fig. 1 (denoted by (i) in the tables). This band of TCHF<sub>3</sub> was not well resolved if moisture was present. In carbon tetrachloride solution this conformer absorbs obviously at  $3580\text{ cm}^{-1}$ , and thus the frequency shift when going from the vapour to  $\text{CCl}_4$  solution is similar for HFP, HFTB, and TCHF<sub>3</sub>.<sup>9,10</sup>

As the wavenumbers of the other two bands are low, these bands obviously belong to conformers where there is intramolecular influence of the  $\text{CCl}_3$  group. As these we propose (ii) a conformer where the OH group lies within

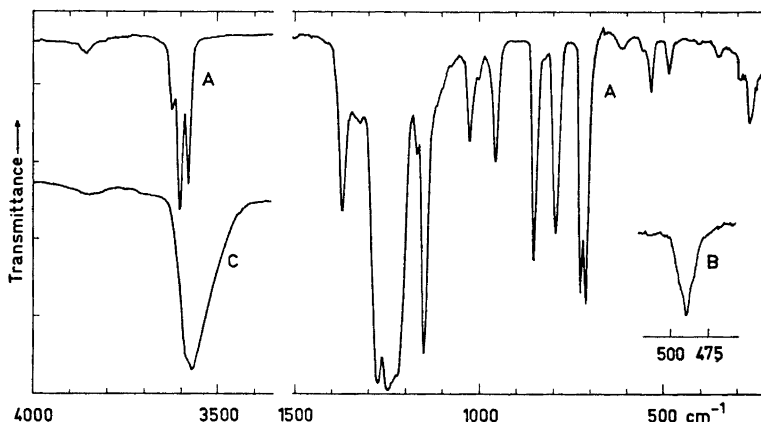


Fig. 2. Infrared spectra of  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ . A, vapour, 1 m cell with CsI windows, pressure about 1 mmHg; B, vapour, path length 1 m, pressure 4 mmHg; C, liquid, between KBr plates.

a  $\text{CF}_3-\text{C}-\text{CCl}_3$  angle and interacts mostly with the  $\text{CF}_3$  group and (iii) a conformer where the OH group lies also within a  $\text{CF}_3-\text{C}-\text{CCl}_3$  angle, but the interaction is mostly with the  $\text{CCl}_3$  group. If the conformer (iii) is close to an eclipsed one, it can be stabilised only by strong  $\text{OH}\cdots\text{Cl}$  interaction. In spectra of solutions of TCHFB in  $\text{CCl}_4$  a broad band that obviously belongs to conformers (ii) and (iii) is centred at  $3553\text{ cm}^{-1}$ . For comparison, it may be mentioned that in  $\text{CCl}_4$  solution trichloroethanol has one band at  $3599\text{ cm}^{-1}$  (gauche conformer),<sup>6</sup> chloral hydrate two bands, at  $3605$  and  $3578\text{ cm}^{-1}$ ,<sup>8</sup>  $\text{CCl}_3\text{C}(\text{CH}_3)_2\text{OH}$  one band at  $3584\text{ cm}^{-1}$ ,<sup>8</sup> and  $(\text{CCl}_3)_2\text{CHOH}$  two bands, at  $3591$  and  $3537\text{ cm}^{-1}$ .<sup>8</sup>

A pair of "satellite" bands are present at  $3852$  and  $3304\text{ cm}^{-1}$  (Fig. 4) in the vapour spectrum of TCHFB (see also the following paper<sup>2</sup>). These are obviously  $3580 \pm \tau\text{OH}$  bands and give for the OH torsion  $\tau\text{OH}$  the value  $274\text{ cm}^{-1}$  (the directly measured value is  $268\text{ cm}^{-1}$ ). The intensity of the sum band is about three times that of the difference band (the theoretical ratio is 3.6). Small amounts of water influence the intensity ratio somewhat; water vapour has a strong absorption band at about  $3850\text{ cm}^{-1}$ . The TCHFB-water complex absorbs at about  $3360\text{ cm}^{-1}$  (vapour phase).

The contour of the OD stretching band of gaseous TCHFB-*d* is similar to that of the OH stretching band of TCHFB (Fig. 3). The triplet is between  $2600$  and  $2700\text{ cm}^{-1}$  in the spectrum of the deuterated compound. The value of the ratio  $\nu\text{OH}/\nu\text{OD}$  is 1.35 as in the case of HFP<sup>9</sup> and PFTB.<sup>2</sup>

The satellite bands are at  $2850$  and  $2440\text{ cm}^{-1}$  in the vapour spectrum of TCHFB-*d*, and thus  $\tau\text{OD} = 205\text{ cm}^{-1}$ . However, in addition to bands due to possible moisture, the overtone bands of the C-F stretching vibrations at  $2300-2500\text{ cm}^{-1}$  make the determination of the position of the  $2440\text{ cm}^{-1}$  band somewhat uncertain.

The spectra of the liquid alcohols indicate that the extent of association is small. The IR (Fig. 2) and Raman (Fig. 3b in the following paper<sup>2</sup>) bands of

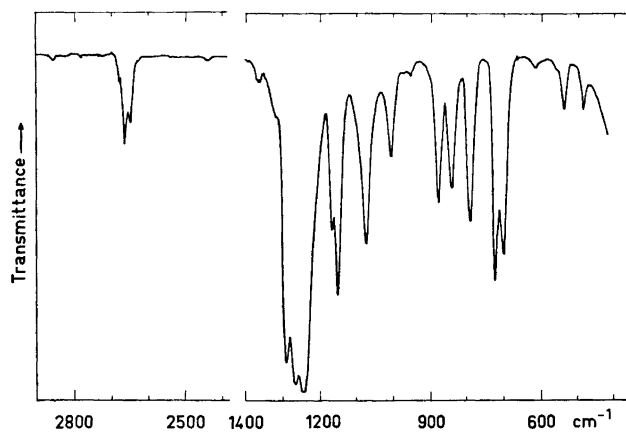


Fig. 3. Infrared spectrum of  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OD}$ . Vapour, 5 cm cell, KBr windows, pressure about 10 mmHg, temperature somewhat above the room temperature.

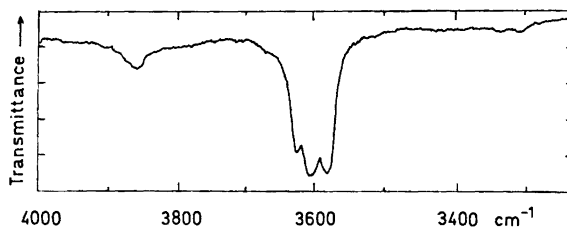


Fig. 4. OH stretching band of  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ . Vapour, 1 m cell with CsI windows.

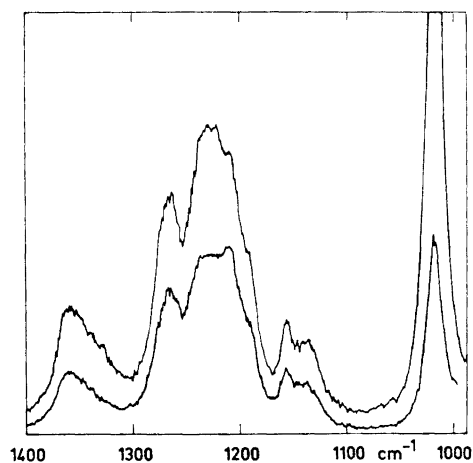
the liquids have similar contours; obviously only two bands corresponding to unassociated alcohol are present. One of these (at  $3585\text{ cm}^{-1}$ ) may be due to conformer (i), the other (at  $3563\text{ cm}^{-1}$ ) to conformers (ii) and (iii). However, the recorded OH stretching bands are broad and asymmetric as there seems to be an additional band on the low-frequency side. This asymmetry may be due to a dimer. If this is true, then the monomer-dimer shift (about  $80\text{ cm}^{-1}$  as in the case of PFTB<sup>2</sup>) would be exceptionally small. The vapour-liquid shift of the OH stretching band of the monomer seems to be about normal.

*COH bending.* The band of the OH in-plane bending ( $\delta\text{OH}$ ) is at  $1330\text{ cm}^{-1}$  in the vapour spectrum<sup>11</sup> and at  $1380\text{ cm}^{-1}$  in the liquid spectrum<sup>12,13</sup> of *t*-butyl alcohol. Fluorination seems to increase the OH bending frequency in the vapour as the band is at  $1350\text{ cm}^{-1}$  in the spectrum of trifluoro-*t*-butyl alcohol, at  $1367\text{ cm}^{-1}$  in the spectrum of HFTB, and at  $1381\text{ cm}^{-1}$  in the spectrum of PFTB.<sup>2,10</sup> The increase may in part be due to intramolecular interaction. This band is obviously at  $1370\text{ cm}^{-1}$  in the spectrum of TCHFb, for it disappears on deuteration and a similar new band appears at  $1075\text{ cm}^{-1}$ . A similar shift occurs in the spectrum of PFTB.<sup>2</sup>

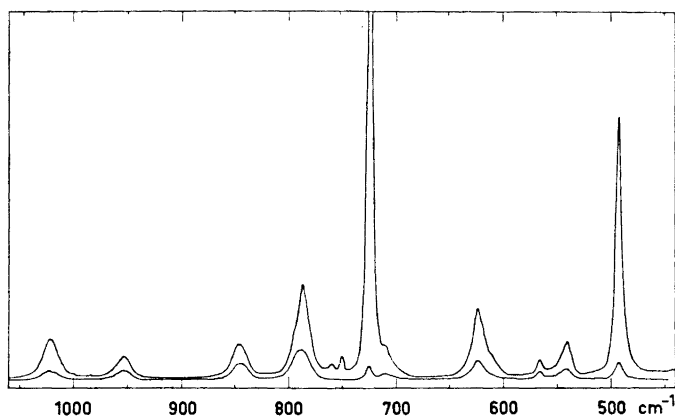
*C–F stretchings.* According to  $C_s$  symmetry, there should be six C–F stretching fundamental bands ( $3a' + 3a''$ ) in the spectra of TCHFb. The C–F stretching bands are usually found between  $1100$  and  $1350\text{ cm}^{-1}$  and are weak in Raman spectra and very strong in IR spectra. Fig. 5a shows that the depolarization ratios of these bands are always relatively high. The most intense Raman C–F stretching band, which also has the lowest depolarization ratio, is that at  $1227\text{ cm}^{-1}$ ; this obviously arises from the symmetric vibration where all C–F bonds stretch in concert. The maximum C–F stretching intensity occurs at about  $1290\text{ cm}^{-1}$  in the Raman spectrum of TCHFb-*d*. The most intense IR band is at  $1243\text{ cm}^{-1}$  in the spectra of gaseous TCHFb and TCHFb-*d*.

*C–Cl stretchings.* Three C–Cl stretching fundamentals are expected. Two of them are found between  $650$  and  $850\text{ cm}^{-1}$  and the third at about  $440\text{ cm}^{-1}$  in the spectra of  $\text{CCl}_3\text{NO}_2$ <sup>14</sup> and  $\text{CCl}_3\text{CHO}$ .<sup>15</sup> The last-mentioned fundamental gives rise to the most intense and highly polarized band in the Raman spectrum; this band is weak in the IR spectrum. The same applies to the band at  $410\text{ cm}^{-1}$  in the spectra of liquid TCHFb. However, Holmes and Fild<sup>16</sup> assign a similar band at  $409\text{ cm}^{-1}$  in the spectrum of  $\text{CCl}_3\text{PF}_4$  to a  $\text{CCl}_3$  defor-

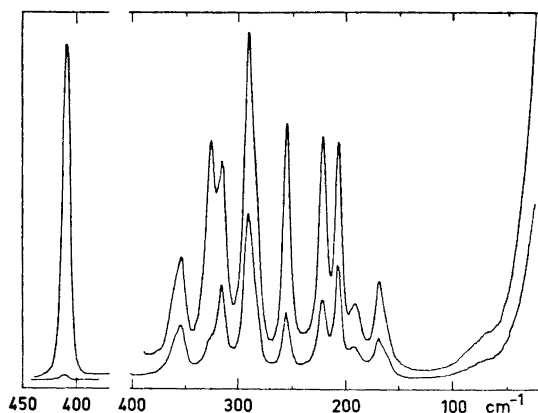




*Fig. 5. a.* The region 1400–1000  $\text{cm}^{-1}$  in the Raman spectrum of liquid  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ . The sensitivity of the detector was five times greater than the sensitivity when the spectra in *b* and *c* were recorded. *b.* The region 1050–450  $\text{cm}^{-1}$  in the Raman spectrum of liquid  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ . *c.* The region 450–50  $\text{cm}^{-1}$  in the Raman spectrum of liquid  $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ . When the band at 410  $\text{cm}^{-1}$  was recorded, the sensitivity was one fifth of that when the other bands were recorded.



*Fig. 5b.*



*Fig. 5c.*

mation vibration. The band of TCHFB at  $850\text{ cm}^{-1}$ , which we interpret as a C-Cl stretching band, may also be due to skeletal stretch.

*Skeletal vibrations.* TCHFB should have four skeletal stretching ( $3a' + a''$ ) and five skeletal bending vibrations ( $3a' + 2a''$ ). It is, however, well known<sup>12,17</sup> that these vibrations are sometimes difficult to identify because of strong coupling effects. This is true also for the C-O stretching vibration band, which may be at  $1026\text{ cm}^{-1}$  in the vapour spectrum of TCHFB; this is a polarized band and shifts to  $1008\text{ cm}^{-1}$  on deuteration.

There is a band due to the most symmetric skeletal stretching between  $700$  and  $800\text{ cm}^{-1}$  in the spectra of highly fluorinated alcohols. It is intense and highly polarized in the Raman spectra and weaker in the IR spectra. This band is at  $725\text{ cm}^{-1}$  in the spectrum of TCHFB.

The band at about  $950\text{ cm}^{-1}$  in the spectra of TCHFB is obviously also a skeletal stretching band. On deuteration, it seems to shift to  $880\text{ cm}^{-1}$ . A similar shift occurs also in the spectra of PFTB<sup>2</sup> and HFTB.<sup>10</sup>

We assign the band at about  $328\text{ cm}^{-1}$  in the spectra of TCHFB and TCHFB-*d* to the  $\text{CF}_3\text{-C-CF}_3$  bending (*cf.* also Refs. 2, 9, and 10). The band at  $490\text{ cm}^{-1}$  is obviously a skeletal bending band, but it is uncertain whether it is to be ascribed mainly to C-O bending or to the most symmetric bending of the  $\text{C}_3\text{CO}$  skeleton.

*CF<sub>3</sub> bendings.* There should be six  $\text{CF}_3$  bending bands ( $3a' + 3a''$ ), but a smaller number is found. By analogy with HFP, we consider the bands at  $711$ ,  $623$ ,  $563$ , and  $541\text{ cm}^{-1}$  to be  $\text{CF}_3$  bending bands. It is possible that the band at  $541\text{ cm}^{-1}$  corresponds to two superimposed fundamentals and the sixth band is too weak to be seen.

*The region below  $320\text{ cm}^{-1}$ .* In this region there are probably three  $\text{CCl}_3$  bending, two  $\text{CCl}_3$  rocking, four  $\text{CF}_3$  rocking, and two  $\text{CF}_3$  torsion bands. Furthermore there are one OH (OD) torsion and one  $\text{CCl}_3$  torsion band.

There is a  $\text{CF}_3$  rocking band at about  $170\text{ cm}^{-1}$  in the Raman spectra of HFP,<sup>9</sup> HFTB,<sup>10</sup> and PFTB,<sup>2</sup> and thus we assign the band at  $170\text{ cm}^{-1}$  in the Raman spectrum of TCHFB to  $\text{CF}_3$  rocking. The band at  $295\text{ cm}^{-1}$  has a shoulder at about  $287\text{ cm}^{-1}$  (Fig. 5c); the latter is due either to a fundamental or to the isotope effect of chlorine. In the latter case, the bands must be due to a  $\text{CCl}_3$  bending fundamental. However, it is probable (*cf.* HFP<sup>9</sup> and PFTB<sup>2</sup>) that one  $\text{CF}_3$  rocking band is at about  $290\text{ cm}^{-1}$ .

The OH and OD torsion (out-of-plane bending) bands were discussed already in connection with the OH stretching.

The weak, broad Raman band at  $70\text{ cm}^{-1}$  may possibly be due to  $\text{CHal}_3$  torsions.

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