

Fluoroalcohols

Part 18.¹ Infrared and Raman Spectra of the Perfluorinated *t*-Butyl Alcohols $(\text{CF}_3)_3\text{COH}$ and $(\text{CF}_3)_3\text{COD}$

JUHANI MURTO, ANTTI KIVINEN*, JOUKO KORPPI-TOMMOLA,
REA VIITALA and JOUKO HYÖMÄKI

*Department of Physical Chemistry, University of Helsinki, Meritullinkatu 1 C,
Helsinki 17, Finland*

The infrared spectra of gaseous, liquid and solid perfluoro-*t*-butyl alcohol, $(\text{CF}_3)_3\text{COH}$, and of its gaseous and liquid deuterated analogue have been recorded, the spectrum of the former alcohol also in an argon matrix. Raman spectra of the liquid compounds have been studied. A spectral assignment is made. Raman spectra of solutions of $(\text{CF}_3)_3\text{COH}$ in carbon tetrachloride and dimethyl sulphoxide and the IR spectrum in carbon tetrachloride are reported. Only one conformer seems to be present to a significant extent in perfluoro-*t*-butyl alcohol. The extent of association is relatively small even in the neat liquids. In the spectrum of gaseous $(\text{CF}_3)_3\text{COH}$, there are two satellite bands displaced by $\pm 255 \text{ cm}^{-1}$ from the OH stretching band; these are due to combinations with OH torsion. No association band of OH bending was found.

Perfluorinated *t*-butyl alcohol, $(\text{CF}_3)_3\text{COH}$ (PFTB), is an interesting compound as it is the most highly fluorinated aliphatic alcohol (perfluorinated primary and secondary alcohols are not stable compounds) and also as its $\text{p}K_a$ is about 5.4 at 25° ,² *i.e.*, the alcohol is almost as strong an acid as acetic acid. We have measured its infrared and Raman spectra together with those of the other highly fluorinated alcohols hexafluoro-2-propanol (HFP)^{3,4} and 2-trichloromethyl-1,1,1,3,3,3-hexafluoro-2-propanol (TCHF₃B).¹ The results are reported in the present paper together with data for $(\text{CF}_3)_3\text{COD}$ (PFTB-*d*). A study of the less fluorinated *t*-butyl alcohols, trifluoro-*t*-butyl alcohol and hexafluoro-*t*-butyl alcohol (HFTB), is in progress.⁵

PFTB was first synthesized by Knunyants and Dyatkin.⁶ Dear *et al.*⁷ studied its lithium, sodium, and potassium salts and Sherry⁸ investigated by calorimetric methods its complex formation with various proton acceptors.

* Department of Pharmacy, University of Helsinki, Fabianinkatu 35, Helsinki 17, Finland.

Table 1. IR and Raman spectra (values of ν/cm^{-1}) of $(\text{CF}_3)_3\text{COH}$ (PFTB). Relative Raman intensities are given in parentheses (the intensity of the band at $770\text{ cm}^{-1}=100$). P=polarized (depolarization ratio $\lesssim 0.7$) and DP=depolarized band; the figures after these are the depolarization ratios. ν =stretching, δ =bending, ρ =rocking and τ =torsion; sh=shoulder. Subscript s=symmetric, a=antisymmetric vibration.

Vapour IR	IR	Liquid Raman		Solid 200 K	20 K, Ar matr. ^a	Assignment ^b
7120 vvw						2 × 3630
3988 vvw						3630 + 357
3956 vvw						3630 + 328
3885 vw	3864 vw					3630 + 252
3691 vvw						3630 + 70; 3 × 1260
3634 sh ^c	3616 m	3616 (3)	P 0.1		3608 m	$\nu_s\text{OH}$, monomer
3630 s						
3626 sh ^c						
	~ 3600 sh	3604 sh (1)	P 0.1	3585 vvw		$\nu_s\text{OH}$, linear dimer end group
3570 sh?	3530 w	3535 (0.7)	P 0.2	3425 br,m	3490 w	3630 - 70, 3 × 1209
						$\nu_s\text{OH}$, oligomer
3375 vvw						3630 - 252
2750 vvw	2750 vvw					2 × 1381
2574 vvw	2564 vvw					2 × 1313
2521 vvw	2515 vvw					2 × 1288
2457 vw	2444 vw					2 × 1260
2369 vw	2359 vw					2 × 1209
2338 vvw	2345 sh					1157 + 1209
2287 vvw	2280 vvw					2 × 1157
2175 vvw	2170 vvw					979 + 1209
2125 vvw	2115 vvw					955 + 1157
2090 vvw	2082 vvw					771 + 1313
2026 vvw	2030 br, vvw					771 + 1260
1925 vw	1918 vvw					2 × 979
1875 vvw	1871 vvw					2 × 955
1810 vvw	1800 vvw					488 + 1313
1780 vvw	1765 vvw					535 + 1260
1725 vvw	1720 vvw					955 + 771
1640 vvw	1634 vvw					357 + 1313
1615 vvw	1590 vvw					488 + 1157
1535 vvw	1535 vvw					535 + 979
1462 vvw	1455 vvw					2 × 771
1381 m	1380 m	1380 (0.6)	P 0.4	1381 m	1382 m	$\delta_s\text{OH}$
1340 sh				1340 vw		357 + 979
					1319 s	
1313 vs	1312 vs	1316 (2)	P 0.35	1311 s	1312 s	$\nu_s\text{CF}_3$
		1298	P		1303 m	328 + 979
1288 sh	1282 sh			1281 sh,s	1292 vvs	$\nu_a\text{CF}_3$
					1280 m	2 × 650
					1272 vs	
1270 sh	1270 sh	1270	P 0.5	1266 sh	1269 vvs	$\nu_s\text{CF}_3$
					1261 vs	
					1257 vs	
1260 vvs	1250 vvs	1250 (1)	P 0.5	1251 vvs	1254 vvs	$\nu_s\text{CF}_3$
				1217 sh	1227 w	488 + 730
					1209 w	
1209 m	1205 m	1210 (0.6)	DP 0.7	1200 sh	1207 m	$\nu_a\text{CF}_3$
					1199 w	

Table 1. Continued.

1157 vs	1147 } vs	1144 (0.3)	DP 0.7	1151 sh	1186 w	
1145 sh?	1134 }			1136 s	1155 vvs	$\nu_s \text{CF}_3$
1060 vvw					1145 w	
979 s	978 s	975 (0.1)	DP	981 s	1133 vw	2×572
958 sh	957 s	960 (0.2)	P 0.4	965 s	1060 m	2×535
955 s					984 sh	ν_a skel., assoc.?
854 vw	852 vvw				981 vs	ν_a skel.
776)					960 br,w	ν_s skel., assoc.?
771 } vw	770 w	770 (100)	P 0.01	771 w	954 s	ν_s skel.
766)					857 vw	ν_s skel.? ^d
733 sh)					769 vw	ν_s skel.
730 } s	729 s	730 (0.1)		729 s	727 s	$\delta_a \text{CF}_3$
727 sh)						
650 vw	649 vw	650 (4)	P 0.4	650 vvw		$\delta_s \text{CF}_3$
572 vvw	571 vvw	572 (0.6)	DP 0.8			$\delta_a \text{CF}_3$
540 sh)	537 m	536 (3)	DP 0.7	535 w		$\delta_s \text{CF}_3$
535 w)						$\delta_a \text{CF}_3$
488 w	488 w	489 (2)	P 0.01			δ_s skel.
		440 (0.2)	P 0.1			δ_s skel.?
357 vw	362 ^f	357 (8)	DP 0.8			δ_a skel.
328 vvw	330 ^f	325 (20)	P 0.3			δ_s skel.
316 vvw	318 vvw ^f	^e				$\rho_a \text{CF}_3$?
285 sh	288 ^f	292 sh	P			$\rho_s \text{CF}_3$
273 sh	^f	280 (0.1)	DP			$\rho_a \text{CF}_3$
252 w,br	^f					$\tau_a \text{OH}$
		242 (0.1)	P 0.2			$\rho_s \text{CF}_3$
195 vvw		199 (0.5)	P ~0.01			$\rho_s \text{CF}_3$
165 sh		170 (0.4)	DP 0.8			$\rho_a \text{CF}_3$
		~70 (0.1)				τCF_3 ?

^a M/A ratio 1000, 2 μmol of PFTB deposited. All weak bands are not given as the alcohol possibly contained some of the decomposition product. ^b The wavenumbers refer to the vapour. ^c These shoulders were seen when the cell was cooled with Dry Ice. ^d This band may be due to the decomposition product. ^e A band may be superimposed by the band at 325 cm^{-1} . ^f It was difficult to obtain reliable IR data below 400 cm^{-1} because of the great volatility of PFTB.

EXPERIMENTAL

Chemicals. PFTB was synthesized by fluorination of TCHFB with SbF_5 according to Dear.⁹ It boiled between 45 and 47° and melted at -17°. The ¹⁹F NMR singlet was at 74.4 ppm relative to CFCl_3 ($\text{CFCl}_2\text{CF}_2\text{Cl}$ as internal standard); Dear reported the value 74.5 ppm.

It was found that PFTB decomposes slowly on standing and that the decomposition product has a higher boiling point. The vapour of the distillation residue of a sample that had stood about half a year at room temperature gave new IR bands at 3592, 1180 sh, 1090, 1035, 915, 850 (also PFTB may have a weak band at about 850 cm^{-1}) and 755 cm^{-1} (the depolarization ratio of the last-mentioned band in the Raman spectrum was 0.01). Of the new bands, those at 1035, 850, and 755 cm^{-1} were the most intense ones (possible new bands between 1200 and 1300 cm^{-1} were not seen because of strong absorption by PFTB). All spectra except the matrix isolation spectrum were recorded on freshly distilled samples.

PFTB is completely miscible with CCl_4 at room temperature. The cloud point of a 33.6:66.4 (w/w) mixture of PFTB and CCl_4 is 6.3°.

Table 2. IR and Raman spectra of $(CF_3)_3COH$ in solutions in dimethyl sulphoxide (DMSO) and CCl_4 . All fundamentals are not included because of solvent bands.

IR 6.9 wt. % in CCl_4	35 wt. % in CCl_4	Raman		41 wt. % in DMSO	Assignment ^a
3610 m ^b	3606 sh	P		^c	} νOH , monomer
3574 m	3578	P		^c	
3500 sh (asym.)					νOH , dimer
1452 vvw					2 × 771
1376 m	1376	P		^d	$\delta_s OH$
1341 sh					357 + 979
1309 vs	1313	P		^d	$\nu_s CF_3$
	1300	P	1296 sh	P	
1278 sh	1275 br	DP	1275	DP	$\nu_a CF_3$
1256 vvs	1256	P	1241		$\nu_s CF_3$
			1226		488 + 730
1203 m	1208	DP	1179	DP	$\nu_a CF_3$
1195 sh					
1151 vs	1143	DP	1138	DP	$\nu_s CF_3$
1140 sh					
				^e	
976 s					ν_a skel.
953 s					ν_s skel.
849 vw ^d	^d			^d	ν_s skel.?
727 vs ^d	^d			^d	$\delta_a CF_3$
647 vw	649	P		^d	$\delta_s CF_3$
	572	DP	573		$\delta_a CF_3$
536 w	538	DP			$\delta_s CF_3, \delta_a CF_3$
487 vw	^d		488		δ_s skel.
			205		$\rho_s CF_3$
	170		^d		$\rho_a CF_3$

^a Vapour frequencies. ^b Not seen in a 0.9 M solution, is seen as a shoulder in a 1.8 M solution, and is the most intense OH stretching band in a 3.6 M solution. ^c In DMSO, the OH stretching band is very broad without any definite maximum. ^d Solvent bands may be present in this region. ^e The SO stretching band (which is at 1045 cm^{-1} in pure DMSO) has split into a doublet with components at 1059 and 1020 cm^{-1} (see also spectra of HFP³ and TCHFB¹).

As the solubility of PFTB in water is very low (a few per cent at most at 100°), deuteration of the hydroxyl group was carried out by shaking PFTB several times with D_2O and finally distilling.

Recording of spectra. The experimental conditions were similar to those employed previously.¹ Most IR spectra were recorded with a Perkin-Elmer 621 spectrometer (the overtone band of OH stretching was measured with a Beckman DK-2A spectrophotometer and some low-frequency gas spectra with a Perkin-Elmer Model 180 spectrometer at the University of Turku, Finland). A 10 cm gas cell, a 5 cm variable temperature gas cell, both with KBr windows, or a 1 m gas cell with CsI windows was used when recording the vapour spectra. The cells were filled to a suitable pressure using a vacuum line. In some cases, the cells were cooled with Dry Ice.

Liquid and solid spectra were recorded employing sealed cells of type FH-01K (RIIC). The spectrum of solid PFTB was obtained with a variable temperature unit VLT 2 (from RIIC) equipped with NaCl windows. The cell containing the liquid was cooled with a mixture of Dry Ice and acetone and the spectrum was recorded without annealing the sample. The matrix isolation spectrum was kindly recorded by Dr. A. J. Barnes at the University College of Swansea (see Ref. 10 for experimental details).

Table 3. The most important bands in the IR and Raman spectra of $(CF_3)_3COD$ (PFTB-d). Relative Raman intensities are given in parentheses.

Vapour IR	IR	Liquid Raman			Assignment
2860 vvw					2680 + 188
2684 sh					$\nu_s OD$, monomer
2680 } s	2668 m	2668	P	0.1	
2676 sh					
	2658 sh	2658 sh	P	0.1	
	2610 br	2600 br	P		$\nu_s OD$, dimer
		1326 (3)	P	0.6	$\nu_s CF_3$
1313 vvs	1311 vs	1305 sh			$\nu_s CF_3$
1296 vs	1288 vs	1295 sh	DP		$\nu_a CF_3$
1268 vs	1256 vvs	1260 (1)	P		$\nu_s CF_3$
1245 sh					
1196 s		1195	DP		$\nu_a CF_3$
1169 vs	1165 vs	1145 (0.4)			$\nu_s CF_3$
1063 vs	1058 vs	1060 (0.2)			$\delta_s OD$
979 vs	978 s				ν_a skel.
958 sh ^a					ν_s skel.?
864 m	860 m				ν_s skel.
775					
771 } vw	770 w	770 (100)	P	0.01	ν_s skel.
765					
733 sh					
730 } vs	725 vs	725 (0.1)		> 0.5	$\delta_a CF_3$
727 sh					
641 vw	643 vw	643 (5)	P	0.4	$\delta_s CF_3$
570 vvw		574 (1)	DP	0.8	$\delta_a CF_3$
540 sh					$\delta_s CF_3$
535 w	534 w	540 (4)	DP	0.7	$\delta_a CF_3$
483 w	483 w	489 (3)	P	0.01	δ_s skel.
356 vw		359 (8)	DP	0.8	δ_a skel.
328 vvw		330 (20)	P	0.3	δ_s skel.
318 vvw		^b			$\rho_a CF_3?$
273 vw		280 (0.1)	DP	0.7	$\rho_a CF_3$
		199 (0.5)	P	0.1	$\rho_s CF_3$
188 w,br					$\tau_a OD$
165 sh?		169 (0.5)	DP	0.8	$\rho_a CF_3$
		70			$\tau CF_3?$

^a The band may be due also to the undeuterated compound. ^b Possible band not seen because of the band at 330 cm^{-1} .

The Raman spectra were measured with a Jarrell-Ash 25-305 spectrometer equipped with an Orlando Model 400 MG Ar/Kr ion laser of 2 W total efficiency. The exciting line used was the 488 nm line of argon. A slit servo system kept the spectral slit width constant at about 2 cm^{-1} and thus permitted the evaluation of relative band intensities. A liquid multipass cell was used in most cases.

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

RESULTS AND DISCUSSION

The PFTB molecule has 39 normal vibrations, 22 of species a' and 17 of species a'' (point group C_s), similarly as *t*-butyl alcohol (the symmetry coordinates of the latter have been published by Tanaka¹¹). However, the hydroxyl proton would be expected to perturb the $(CF_3)_3CO$ group (symmetry C_{3v}) only slightly (*cf.* Ref. 12). Thus the PFTB molecule can be considered to give rise to 24 fundamentals based on the C_{3v} symmetry and three additional fundamentals that are due to the OH proton. The spectrum of PFTB is indeed much simpler and the number of found fundamentals less than in the spectrum of TCHF₃,¹ where we expect to find all 39 fundamentals. All vibrations of point groups C_s and C_{3v} are IR and Raman active, except those of species a_2 (C_{3v}) which are inactive in both cases.

The principal axes and moments of inertia were computed by the programme CART written by Schachtschneider.¹³ The following values of structural parameters were used: $r(C-F) = 1.33$ Å, $r(C-C) = 1.53$ Å, $r(C-O) = 1.42$ Å, $r(O-H) = 0.98$ Å, $\angle COH = 106^\circ$, all other angles tetrahedral. These values were chosen on the basis of Refs. 14–16 as there are no reports on the structure of PFTB. As the angles C–C–F were within $\pm 2^\circ$ of the tetrahedral in all references quoted, the tetrahedral angle was used. The angles C–C–C are possibly slightly greater than tetrahedral, but the angle was taken to be tetrahedral also in these cases. After this work had been completed, a report on the structure of the compound $(CF_3)_3CH$ was published.¹⁷

If we assume, in the first place, that the CF_3 groups are fixed with one C–F bond parallel to the C–O bond, there are six fluorine atoms in a plane, and we could consider two types of conformers: (i) one type where the O–H and C–C bonds are eclipsed (conformers of this type are usually energetically less favoured; see Ref. 18 concerning *t*-butyl alcohol) and (ii) another type where the O–H and C–C bonds are staggered. The intramolecular distance from the hydrogen atom to the nearest two fluorine atoms is 2.35 Å in the former and 2.39 Å in the latter case, *i.e.*, the distances are practically equal. However, an electron-diffraction study of the $(CF_3)_3CH$ molecule shows that the CF_3 groups are engaged in a rather large libration type of motion around the C–C bonds, and the mean angle of torsion is 18° . Two more factors operate in PFTB than in $(CF_3)_3CH$, *viz.*, intramolecular OH...F attraction and the repulsion between the fluorine atoms and the lone electron pairs of oxygen. The energetically most favoured conformer of PFTB may be somewhat similar to type (ii) with slightly rotated CF_3 groups.

The principal moments of inertia are $I_A = 598.0$, $I_B = 598.9$, and $I_C = 817.0$ amu Å² for both possible conformers of PFTB, and $I_A = 602.6$, $I_B = 604.4$, and $I_C = 818.0$ amu Å² for PFTB-*d*. The molecules are thus very nearly oblate symmetric tops. The C axis is very close to and almost parallel with the C–O bond axis.

As the molecules are almost symmetric tops, “parallel” and “perpendicular” bands are expected to occur in the vapour spectra. The formulae of Gerhard and Dennison¹⁹ give for the P–R separation of parallel bands of PFTB the value 10.6 cm⁻¹ (at 300 K). The band at 771 cm⁻¹ (Fig. 4D) is unquestionably of this type; the P–R separation is 10 cm⁻¹. The OH stretching is obviously

an example of a nearly perpendicular vibration; the band is seen in Fig. 4A. The band at 730 cm^{-1} has a similar contour. The band at 1157 cm^{-1} is almost triangular (however, it is a doublet in the IR spectrum of the liquid).

OH (OD) stretching. In agreement with the above discussion, there was experimental evidence that only one conformer predominates in the vapour. The OH stretching band is at 3630 cm^{-1} (HFP³ has a band at 3626 cm^{-1} and HFTB⁵ at 3623 cm^{-1}) and the OD stretching band at 2680 cm^{-1} ; the ratio of these wavenumbers is 1.35. On each side of the OH stretching band and $\pm 255\text{ cm}^{-1}$ away from it there are two prominent satellite bands (Fig. 5). These are found also in spectra taken employing a 100 m path length cell (pressure of PFTB 0.15 mmHg) and must thus be due to the monomer. They are obviously the sum and difference combinations of OH stretching with a fundamental at about 255 cm^{-1} ; the latter must be the OH torsion. The in-

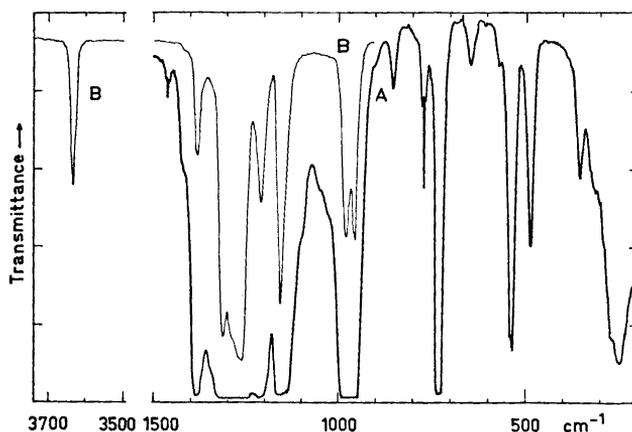


Fig. 1a. IR spectra of gaseous $(\text{CF}_3)_3\text{COH}$. A, 1 m cell, pressure 6 mmHg. B, 10 cm cell, pressure 4 mmHg.

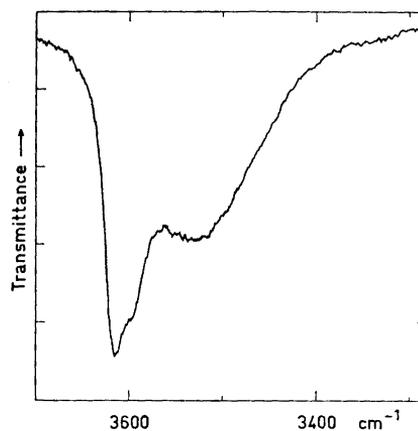


Fig. 1b. IR spectrum of liquid $(\text{CF}_3)_3\text{COH}$ in the OH stretching region. Cell thickness 0.02 mm.

tensity of the sum band is about 2.5 times that of the difference band; the theoretical ratio is 3.3. Small amounts of water present may influence the difference band; the spectrum of a gaseous PFTB–water mixture showed an intense complex band at about 3360 cm^{-1} . It is interesting that only one pair of prominent satellite bands is observed in the spectrum of PFTB, as there are usually several such pairs in the spectra of other alcohols (this is seen clearly in the vapour spectra of 2,2,2-trifluoroethanol²⁰ and HFP³). The other satellite bands around the OH stretching band in the spectrum of PFTB are much weaker.

The OD stretching band (Fig. 2) is in the region of C–F stretching overtones and it is thus more difficult to locate the satellite bands in this case. There are

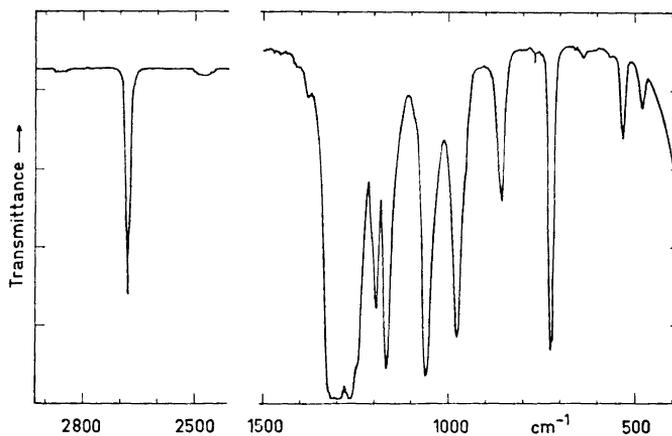


Fig. 2. IR spectrum of gaseous $(\text{CF}_3)_3\text{COD}$, 10 cm cell, pressure 10 mmHg.

bands $\pm 180\text{ cm}^{-1}$ ($255/\sqrt{2}=180$) from the OD stretching band that might be the $\nu\text{OD} \pm \tau\text{OD}$ bands (from the far-infrared spectrum of gaseous PFTB-*d* we obtain the value 188 cm^{-1} for the OD torsion band).

Inspection of the IR and Raman spectra of the neat liquids (Figs. 1b and 3b) reveals that the extent of association of PFTB is relatively small when compared with that of, *e.g.*, *t*-butyl alcohol, but clearly greater than that of TCHFb. We estimate that roughly 70–80 % of PFTB is in the monomeric form. The dimerization constant cannot be measured by the method used previously,²¹ as this presupposes that the molar absorption coefficient of the monomer remains constant with increasing alcohol content of the solution, which is true only in dilute solutions. It has been found previously²² that the dimerization constant of fluorinated *t*-butyl alcohols decreases with increasing number of fluorine atoms in the molecule.

The value of the monomer-dimer shift, about 80 cm^{-1} , is relatively small.²² There is a shoulder on the low-frequency side of the monomer band in the spectra of liquid PFTB (Figs. 1b and 3b) that probably is due to a terminal OH group of a linear dimer.

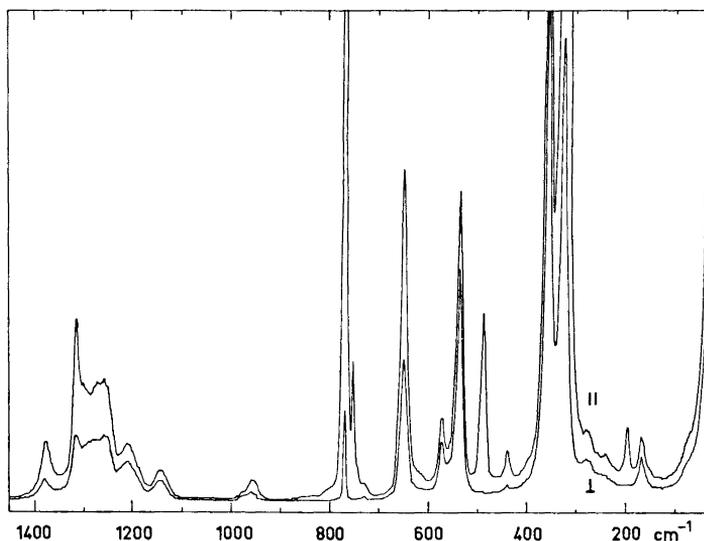


Fig. 3a. Raman spectrum of liquid $(\text{CF}_3)_3\text{COH}$, region $1400-0 \text{ cm}^{-1}$.

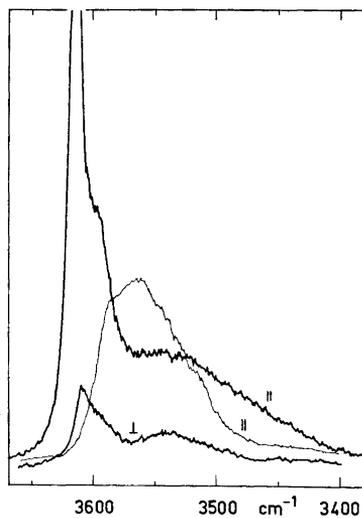


Fig. 3b. Raman spectra in the OH stretching region of liquid $(\text{CF}_3)_3\text{COH}$ (thick line) and liquid $\text{CCl}_3\text{C}(\text{CF}_3)_2\text{OH}$ (thin line). The sensitivity was five times greater than the sensitivity when Fig. 3a was recorded.

In the spectrum of a dilute solution of PFTB in CCl_4 , the OH stretching band is at 3574 cm^{-1} ; with increasing concentration a shoulder appears at 3610 cm^{-1} . This cannot be due to a terminal OH group as the extent of dimer formation must still be low. This concentration dependence of the bands is exceptional and indicates a specific interaction between PFTB and CCl_4 molecules. Tamborski *et al.*²³ found a similar effect in spectra of aromatic

perfluorinated *t*-butyl alcohols in CCl_4 . Also Sherry⁸ proposed a specific interaction to occur between PFTB and CCl_4 to explain his calorimetric results.

No "fingers" are found on the low-frequency side of the OH stretching band of liquid and solid PFTB and liquid TCHF_B; such intense bands have been observed in spectra of phenol²⁴ and HFP³ and they are absent from the vapour spectra.

Only one conformer seems to dominate also in the argon matrix.

OH (OD) bending. The δOH band of tertiary alcohols is usually above 1300 cm^{-1} .²⁵ It is obviously at 1381 cm^{-1} in the spectrum of gaseous PFTB as it shifts to 1063 cm^{-1} on deuteration (simultaneously it gains in intensity). The frequency ratio is thus 1.30. In the vapour spectrum of TCHF_B the OH bending band was at 1370 cm^{-1} and on deuteration it shifted to 1075 cm^{-1} .¹ Fluorination of *t*-butyl alcohol increases the value of the OH bending frequency.^{5,1} The OH and OD bending bands seem not to be influenced by aggregation, as no characteristic new association bands were found in the spectra of solid and liquid PFTB (although the OH stretching region of the solid indicated

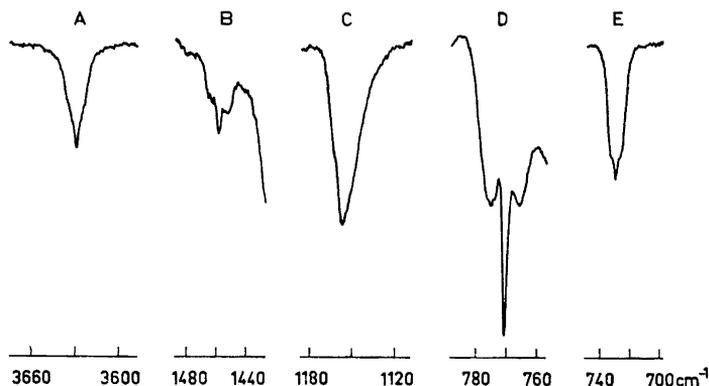


Fig. 4. Band contours in IR spectra of gaseous $(\text{CF}_3)_3\text{COH}$. Bands A, C, and E, 5 cm cell, pressure 5 mmHg. Bands B and D, 1 m cell, pressure 30 mmHg.

only associated PFTB). The situation was similar in the case of the OD bending band of $(\text{CF}_3)_2\text{CHOD}$ at about 1000 cm^{-1} ; the obvious reason for this kind of behaviour is coupling with other vibrations (two OH association bands are seen in the spectra of liquid HFP³). Unfortunately, the OH bending band of PFTB in DMSO could not be seen in the Raman spectrum because of the solvent bands.

C-F stretchings. The representation of the C-F stretching vibrations is $5a' + 4a''$ in point group C_s and $2a_1 + a_2 + 3e$ in point group C_{3v} . As it is expected that the splitting of the degenerate fundamentals is small, there should be six bands due to C-F stretching vibrations in the IR and Raman spectra of PFTB (one of these may be weak in both spectra, as a fundamental of species a_2 is inactive in both cases). The splitting could not be verified even

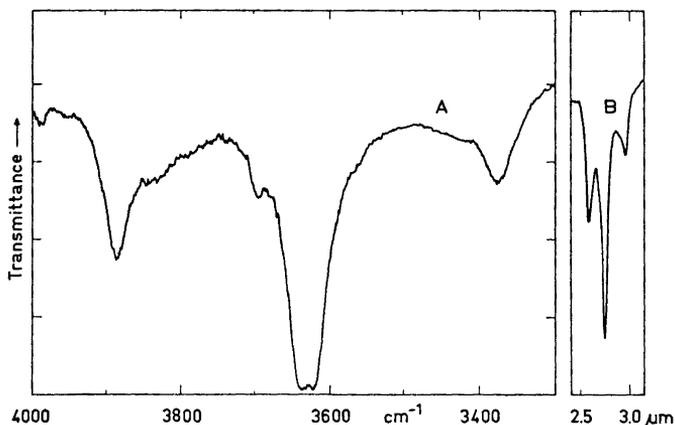


Fig. 5. IR spectrum of gaseous $(\text{CF}_3)_3\text{COH}$ in the OH stretching region showing the satellite bands. A, 1 m cell, pressure 32 mmHg. B, 100 m cell, pressure 0.15 mmHg.

in the matrix spectrum, as there were very many bands in the region in question (Fig. 7).

C-F stretching bands are usually found between 1100 and 1350 cm^{-1} (see, however, Ref. 26). The highest Raman intensity and the lowest depolarization ratio in this region is at 1316 cm^{-1} for PFTB; this band is probably due

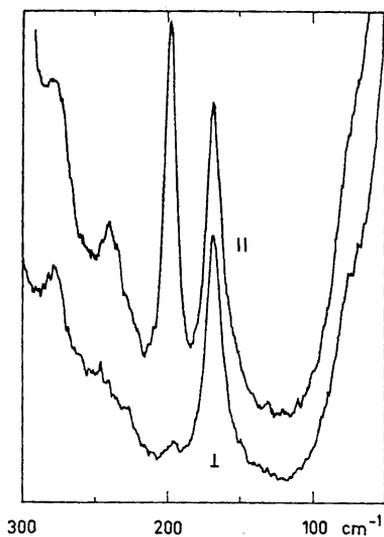


Fig. 6. Raman spectrum of liquid $(\text{CF}_3)_3\text{COH}$ in the low-frequency region.

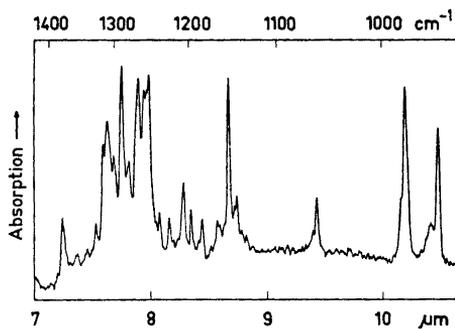


Fig. 7. Part of the IR spectrum of $(\text{CF}_3)_3\text{COH}$ in an argon matrix. $M/A = 1000$, $2\text{ }\mu\text{mol}$ of the alcohol deposited.

to the vibration where all C–F bonds stretch in concert. In the Raman spectrum of PFTB-*d* this band is at 1326 cm^{-1} (no IR band is seen at this position). As usual, the CF_3 stretching Raman bands are weak, and as they are also close together, accurate band positions and depolarization ratios were not obtained.

The wavenumbers of the overtones of many vibrations of PFTB are about 1.96 times those of the fundamentals (this is true also for the OH stretching).

Skeletal stretchings. The representation of the skeletal stretching vibrations is $3a' + a''$ (C_s) or $2a_1 + e$ (C_{3v}). Because of coupling of vibrations in compounds of type $(\text{CX}_3)_3\text{CO}$, it is difficult to find a band that relates essentially to C–O stretching.^{12,27} In the case of PFTB, the band at 771 cm^{-1} (Fig. 4D) can be unequivocally assigned to a symmetric skeletal stretching vibration. It is the most intense band in the Raman spectrum (it is five times as intense as any other band; it gave 10^5 counts s^{-1} with the FW-130 photomultiplier tube and multipass cell and dead-time effects of the detector begin to become significant at such high intensities). It is also completely polarized. There is a similar weak band at 1462 cm^{-1} in the vapour spectrum (Figs. 1 and 4B) that obviously is the overtone band of the symmetric skeletal stretching vibration. The vibration is thus very anharmonic ($1462/771 = 1.896$; the intensity of the 1462 cm^{-1} band is about one fifth of that of the 771 cm^{-1} band). The band (at 770 cm^{-1}) is very sharp in the IR spectrum of the liquid, and the same is true regarding the overtone.

The bands at 955 and 979 cm^{-1} are obviously also skeletal stretching bands. The band at 955 cm^{-1} shifts to 864 cm^{-1} on deuteration. A shift of this kind seems to be characteristic of fluorinated *t*-butyl alcohols.^{1,5} The fourth skeletal stretching band was not found with certainty; the band may also be obscured by the intense C–F stretching bands.

CF_3 bendings. The representation of these is similar to that of the C–F stretchings, and the bands are usually between 500 and 750 cm^{-1} . There are four bands in this region in the spectrum of PFTB that can be assigned with a high degree of certainty as CF_3 bending bands. The assignment is supported by analogy with HFP,³ TCHFB¹ and other compounds.^{15,16} It is possible that two fundamentals may occur at about the same wavenumber, and we consider the shoulder at 540 cm^{-1} in the vapour spectrum to be the fifth bending fundamental band.

Skeletal bendings. Their representation is $3a' + 2a''$ (C_s) or $a_1 + 2e$ (C_{3v}). Three of the bands (at 488 , 357 , and 328 cm^{-1}) can be assigned by analogy with HFP, TCHFB and other compounds with a relatively high degree of certainty. The band at 328 cm^{-1} is obviously due to deformation of the CF_3 –C– CF_3 angle; its position is relatively insensitive to structure.^{1,3,16} The band at 488 cm^{-1} is assigned to the most symmetric (a_1 type) deformation.

CF_3 rockings. The representation is $3a' + 3a''$ (C_s) or $a_1 + a_2 + 2e$ (C_{3v}). The band at 199 cm^{-1} (Raman, liquid; Figs. 3a and 6) obviously relates to the most symmetric rock (a_1 type) as it is completely polarized and no such band is seen in spectra of HFTB and HFP. The assignment of the band at 170 cm^{-1} as a rocking band is also on a firm basis (*cf.* Refs. 1 and 3). The assignments of the bands at 291 and 316 cm^{-1} are the least certain.

OH (OD) torsion (out-of-plane bending). The broad torsion band is seen at 252 cm^{-1} in the IR spectrum of gaseous PFTB; the OD torsion band is at

188 cm^{-1} in the spectrum of gaseous PFTB-*d*. The ratio $\tau\text{OH}/\tau\text{OD}$ is thus 1.34. No association band of the torsions was seen, as is usual with highly fluorinated alcohols.^{3,5}

CF₃ torsions. These bands are obviously at about 50–70 cm^{-1} (*cf.* Ref. 15). The shoulder at about 70 cm^{-1} on the Rayleigh band in the Raman spectra of liquid PFTB and PFTB-*d* may possibly be due to these.

The *t*-perhalogenobutanols will be discussed further by one of us (J. K.-T.) later.

Acknowledgements. Dr. A. J. Barnes (University College of Swansea, Wales) is thanked for the recording of the matrix isolation spectrum and for helpful suggestions, Mr. J. Corbett (Royal Ordnance Laboratory, Bridgwater, England) for recording the gas spectrum with a 100 m path length cell (this was proposed and kindly arranged by Dr. H. E. Hallam, University College of Swansea), Dr. W. A. Thomas (University College of Swansea) for recording the ¹⁹F NMR spectrum, and Dr. J. Kankare (University of Turku, Finland) for checking the wavenumbers of the low-frequency vapour bands with a Perkin-Elmer Model 180 Spectrometer. We gratefully acknowledge financial support from the *Jenny and Antti Wihuri Foundation* (to purchase chemicals) and from the *Finnish National Research Council for Sciences*.

REFERENCES

1. Murto, J., Kivinen, A., Kajander, K., Hyömäki, J. and Korppi-Tommola, J. *Acta Chem. Scand.* **27** (1973) 96. (Part 17.)
2. Dyatkin, B. L., Mochalina, E. P. and Knunyants, I. L. *Tetrahedron* **21** (1965) 2991; Filler, R. and Schure, R. M. *J. Org. Chem.* **32** (1967) 1217.
3. Murto, J., Kivinen, A., Viitala, R. and Hyömäki, J. *Spectrochim. Acta. To be published.*
4. Barnes, A. J. and Murto, J. *J. Chem. Soc. Faraday Trans. 2* **1972**. *In press.*
5. Korppi-Tommola, J. *To be published.*
6. Knunyants, I. L. and Dyatkin, B. L. *Izv. Akad. Nauk SSSR Ser. Khim.* **1964** 923.
7. Dear, R. E. A., Fox, W. B., Fredericks, R. J., Gilbert, E. E. and Huggins, D. K. *Inorg. Chem.* **9** (1970) 2590.
8. Sherry, A. D. *Diss. Abstr.* **B 32** (1971) 3288; *Ph. D. Thesis*, Kansas State University 1971, p. 68; Sherry, A. D. and Purcell, K. F. *J. Am. Chem. Soc.* **94** (1972) 1853.
9. Dear, R. E. A. *Synthesis* **7** (1971) 361.
10. Barnes, A. J., Hallam, H. E. and Scrimshaw, G. F. *Trans. Faraday Soc.* **65** (1969) 3150.
11. Tanaka, C. *Nippon Kagaku Zasshi* **83** (1962) 398.
12. Pritchard, J. G. and Nelson, H. M. *J. Phys. Chem.* **64** (1960) 795.
13. Schachtschneider, J. H. *Technical Report No. 231–64*, Shell Development Co.
14. Boulet, G. A. *Diss. Abstr.* **25** (1964) 3283; Hildebrandt, R. L., Andreassen, A. L. and Bauer, S. H. *J. Phys. Chem.* **74** (1970) 1586; Aziz, N. E. A. and Rogowski, F. *Z. Naturforsch.* **19b** (1964) 967; Buckton, K. S. and Azrak, R. G. *J. Chem. Phys.* **52** (1970) 5652; Prater, B. G. L. *Diss. Abstr.* **B 30** (1970) 5454; Andreassen, A. L., Zebelman, D. and Bauer, S. H. *J. Am. Chem. Soc.* **93** (1971) 1148; Andreassen, A. L. and Bauer, S. H. *J. Chem. Phys.* **56** (1972) 3802.
15. Berney, C. V. *Spectrochim. Acta* **21** (1965) 1809.
16. Miller, F. A. and Kiviat, F. E. *Spectrochim. Acta* **A 25** (1969) 1577.
17. Stølevik, R. and Thom, E. *Acta Chem. Scand.* **25** (1971) 3205.
18. Reece, I. H. and Werner, R. L. *Spectrochim. Acta* **A 24** (1968) 1271.
19. Gerhard, S. L. and Dennison, D. M. *Phys. Rev.* **43** (1933) 197.
20. *E.g.*, Jones, D. *Ph. D. Thesis*, University College of Swansea, University of Wales 1965.
21. Kivinen, A. and Murto, J. *Suomen Kemistilehti* **B 40** (1967) 6.
22. Kivinen, A., Murto, J., Korppi-Tommola, J. and Kuopio, R. *Acta Chem. Scand.* **26** (1972) 904.

23. Tamborski, C., Burton, W. H. and Breed, L. W. *J. Org. Chem.* **31** (1966) 4229.
24. Evans, J. C. *Spectrochim. Acta* **16** (1960) 1382.
25. Stuart, A. V. and Sutherland, G. B. B. M. *J. Chem. Phys.* **24** (1956) 559.
26. Tuazon, E. C., Fateley, W. G. and Bentley, F. F. *Appl. Spectrosc.* **25** (1971) 374.
27. Simpson, D. M. and Sutherland, G. B. B. M. *Proc. Roy. Soc. (London)* **A 199** (1949) 169.

Received June 15, 1972.