

# Infrared, Matrix Infrared and Raman Spectra of Hexafluoro-*tert*-butyl Alcohol and Vibrational Assignment

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Infrared spectra are reported for hexafluoro-*tert*-butyl alcohol and its OD derivative in gaseous, liquid and solid states, in CCl<sub>4</sub> solution and in argon, krypton and nitrogen matrices. The Raman spectra of the liquids and CCl<sub>4</sub> solutions have also been recorded. Two conformers are found in the vapour and liquid states and in CCl<sub>4</sub> solution, while in matrices, two species appear only for the deuterio-alcohol in solid nitrogen. A vibrational assignment is given for the conformer present in most phases. The alcohol dimers seem to have open-chain (non-cyclic) structures in matrices. A non-bonded interaction is proposed as the origin of the end group bands in the matrix spectra of halogenated alcohols.

To complete our study of the conformations, molecular vibrations and association of *tert*-butyl alcohol and a series of its fluorine derivatives, we have recorded infrared and Raman spectra of hexafluoro-*tert*-butyl alcohol (2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol, HFTB). The molecular vibrations<sup>1</sup> and association<sup>2</sup> of *tert*-butyl alcohol (2-methyl-2-propanol, TB) and infrared and Raman spectra of trifluoro-*tert*-butyl alcohol<sup>3</sup> (2-trifluoro-methyl-2-propanol, TFTB) and perfluoro-*tert*-butyl alcohol (PFTB)<sup>4</sup> have recently been reported.

Hexafluoro-2-propanol (HFP) and hexafluoro-*tert*-butyl alcohol are closely related compounds. Since the conformational isomerism<sup>5</sup> and the vibrational spectra<sup>6</sup> of the former have already been studied, it is of interest to see whether the conformers and the association characteristics of the two alcohols are similar.

## EXPERIMENTAL

HFTB was purchased from Pierce Chemical Co., Rockford, Ill., and purified by fractional distillation.<sup>7</sup> The OD derivative was synthesized by shaking the alcohol with D<sub>2</sub>O, collecting the alcohol layer (HFTB and D<sub>2</sub>O are only partly miscible) and distilling the fraction over D<sub>2</sub>SO<sub>4</sub>. After repeating the procedure four or five times the product was more than 95 % isotopically pure.

The infrared spectra were recorded with Perkin-Elmer 180 and 621 spectrometers in the wavenumber regions from 500 to 50 cm<sup>-1</sup> and from 4000 to 200 cm<sup>-1</sup>, respectively.<sup>1</sup> Matrix spectra were obtained in the same way, as previously reported,<sup>3,8</sup> varying the matrix to absorber (M/A) ratio from 5000 to 20. The Raman spectra were recorded with a Jarrell-Ash spectrometer with the 488 nm line of an argon ion laser as the exciting line.<sup>1</sup> Throughout the experiments the spectral slit width was kept constant at about 2.5 cm<sup>-1</sup>. Standard 90 degree excitation was used for most measurements.

## RESULTS AND DISCUSSION

HFTB has 39 modes of vibration, 22 of species *a'* and 17 of species *a''* assuming the point group C<sub>s</sub>. All vibrations are infrared and Raman active, the *a'* species showing polarized bands in the Raman spectra. The most important spectral results and tentative assignments are given in Table 1. A Raman spectrum of liquid HFTB is shown in Fig. 1. Detailed spectroscopic data for HFTB-OD, including the results from argon and nitrogen matrix spectra, are available from the author on request.

*Conformations.* In the vapour phase, the infrared spectrum of HFTB in the  $\nu(\text{OH})$  region

Table 1. The observed infrared and Raman frequencies (cm<sup>-1</sup>) of (CF<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)COH (fundamental regions).

Vapour	Argon matrix IR <sup>a</sup>	Nitrogen matrix IR <sup>a</sup>	Raman liquid <sup>b</sup>	Fund. and species	Tentative assignments <sup>c</sup>		
3656 w		3624 vw	3638 (1) p	$\nu_1, a'$	$\nu(\text{OH}), C_1$ conformer		
3629 sh		3586 as		$\nu_1, a'$	$\nu(\text{OH}), C_s$ conformer		
3624 s	3604 s	3583 s	3610 (2) p				
3617 sh		3579 s					
			3230 (<1) dp		$\nu_{02} + \nu_{36}$		
3035 sh				$\nu_{23}, a''$	$\nu(\text{CH}_3)$		
3028 w	3024 vw	3026 vw	3025 (12) dp				
2973 w	2969 vw	2970 vw	2969 (40) p			$\nu_2, a'$	$\nu(\text{CH}_3)$
2907 vw			2908 (6) p			$\nu_3, a'$	$\nu(\text{CH}_3)$
			2769 (2) p		2 $\nu_5$ FR with $\nu_2$		
1469 sh	1474 vw	1478 vw		$\nu_{24}, a''$	$\nu_{25} + \nu_{37}$		
1465 m	1464 sh	1465 sh					
1459 m	1460 m	1462 m	1468 (4) dp			$\nu_{13} + \nu_{30}$	$\delta(\text{CH}_3)$
1455 sh	1457 sh					$\nu_{28} + \nu_{34}$	$\delta(\text{CH}_3)$
1449 sh	1448 w	1451 w		$\nu_4, a'$	$\delta(\text{CH}_3)$		
1398 m	1395 w	1398 w	1400 (2) p	$\nu_5, a'$	$\delta(\text{CH}_3)$		
	1392 sh				$\nu_{10} + \nu_{37}$		
	1389 vw	1392 w			$\nu_{13} + \nu_{14}$		
1375 sh	1371 vw			$\nu_6, a'$	$\nu_{13} + \nu_{31}$		
	1366 sh	1377 w					
1369 m	1365 w	1375 sh	1375 (<1) p	$\nu_7, a'$	$\nu_{11} + \nu_{20}$		
	1319 as	1329 vw					
1315 s	1316 vs	1318 vs	1316 (2) p	$\nu_8, a'$	$\nu_{12} + \nu_{34}$		
	1309 sh	1311 as					
	1300 sh	1303 sh			$\nu(\text{CF}_3)$		
1294 s	1291 vs	1294 s	1295 (3) p	$\nu_8, a'$	$\nu_{11} + \nu_{37}$		
	1283 w	1290 s					
	1271 sh	1267 w			$\nu_{13} + \nu_{32}$		
	1265 w	1262 w			$\nu_{13} + \nu_{18}$		
1239 sh	1237 vs	1238 s	1240 (as)	$\nu_{25}, a''$	$\nu_{13} + \nu_{16}$		
1233 vs	1229 vs	1230 vs	1225 (3) dp	$\nu_{26}, a''$	2 $\nu_{14}$		
	1224 vs	1224 vs		$\nu_{27}, a''$	$\nu(\text{CCC})$		
	1217 sh	1216 sh			$\nu(\text{CF}_3)$		
	1214 sh	1213 sh			$\nu(\text{CF}_3)$		
	1203 vw	1200 w			2 $\nu_{31}$		
	1197 vw	1197 sh			$\nu_{16} + \nu_{30}$		
	1194 w				$\nu_{12} + \nu_{36}$		
1187 sh	1181 m	1182 vs		$\nu_9, a'$	$\nu_{18} + \nu_{29}$		
1182 vs	1178 vs	1180 vs	1180 (sh) p				
	1174 sh	1173 sh			$\nu_{12} + \nu_{37}$		
	1162 sh	1164 vw		$\nu_{10}, a'$	$\nu_{14} + \nu_{32}$		
1163 sh	1158 s	1158 s	1160 (1) dp				
1101 sh	1113 vw	1111 vw	1109 (as)		$\nu(\text{CCC})$		
1098 vs	1092 vs	1092 vs	1090 (1) dp	$\nu_{28}, a''$	$\nu_{13} + \nu_{35}$		
1093 sh	1086 w			$\nu_{11}, a'$	$\nu(\text{CF}_3)$		
1082 sh	1076 s	1082 s	1080 (as)				
	1062 sh	1067 sh			$\nu_{13} + \nu_{18}$		
	1061 w				$\nu(\text{CO}) + \delta(\text{OH})$		
		964 as	961 (as)		2 $\nu_{32}$		
961 m	958 m	961 w	957 (4) p	$\nu_{12}, a'$	$\nu_{30} + \nu_{34}$		
956 sh		957 sh		$\nu_{29}, a''$	$\varrho(\text{CH}_3)$		
880 sh							
876 m	873 w	875 m	877 (1) dp				
872 sh		869 sh					
P769 sh					$\nu_{16} + \nu_{34}$		
Q765 w					$\varrho(\text{CH}_3)$		
Q763 w	762 w	763 w	766 (99) p	$\nu_{13}, a'$	$\nu_{16} + \nu_{17}$		
					$\nu(\text{CCC})$		

Table 1. Continued.

R758 sh						
P707 sh						
Q702 s	700 s	701 s	705 (1) dp	}	$\nu_{30}, a''$	$\delta(\text{CF}_3)$
R698 sh	698 sh					$\nu_{32} + \nu_{37}$
638 sh				}	$\nu_{14}, a'$	$\nu_{21} + \nu_{33}$
633 m	629 w	631 w	636 (12) p			$\delta(\text{CF}_3)$
624 sh	617 sh	622 sh		}	$\nu_{15}, a'$	$\delta(\text{CF}_3)$
613 w	609 vw	608 vw	613 (7) dp			$\nu_{31}, a''$
606 sh						$\nu_{34} + \nu_{37}$
P539 sh				}	$\nu_{32}, a''$	$\delta(\text{CF}_3)$
Q534 m	533 w	534 w	540 (2) dp			
R530				}	$\nu_{16}, a'$	$\delta(\text{CF}_3)$
517 sh						$\nu_{33}, a''$
512 m	512 m	513 m	520 (6) p	}	$\nu_{34}, a''$	$\tau(\text{OH})$
464 m	464 w	465 m	467 (1) dp			
457 sh				}	$\nu_{17}, a'$	$\delta(\text{CCO})$
367 s	365 sh	454 s	369 (7) dp			$\nu_{35}, a''$
315 w	363 s	443 m	356 (9) dp	}	$\nu_{18}, a'$	$\delta(\text{CCC})$
		432 sh				$\nu_{19}, a'$
	358 sh	362 w	369 (7) dp	}	$\nu_{20}, a'$	$\rho(\text{CF}_3)$
349 m	348 m	353 vw	356 (9) dp			$\nu_{36}, a''$
P336 sh				}	$\nu_{37}, a''$	$\rho(\text{CF}_3)$
Q330 s	329 m	331 vw	336 (sh)			$\nu_{38}, a''$
R325 sh	324 sh	326 vw	330 (17) p	}	$\nu_{31}, a'$	$\rho(\text{CF}_3)$
293 sh						$\nu_{38}, a''$
289 vw	288 vw	289 vw	294 (1) dp	}	$\nu_{38}, a''$	$\tau(\text{CF}_3)$ and $\nu_{22}, a'$
286 sh						
249 vw	245 vw	247 vw	247 (< 1)	}	$\nu_{38}, a''$	$\tau(\text{CF}_3)$ and $\nu_{22}, a'$
235 vw	235 vw	235 vw				
			221 (< 1)	}	$\nu_{31}, a'$	$\rho(\text{CF}_3)$
170 $d_{\text{vw}}$			173 (1) p			$\nu_{38}, a''$
91 $d_{\text{br}}$			102 (br)		$\nu_{38}, a''$	$\tau(\text{CF}_3)$ and $\nu_{22}, a'$

<sup>a</sup> The intensities refer to matrices with large M/A ratios. <sup>b</sup> Relative intensities are given in parenthesis. The letters p or dp after the parenthesis refer to depolarization ratios. <sup>c</sup> The assignments of combination bands should be taken as informative only. <sup>d</sup> From far-infrared spectrum (Perkin-Elmer 180 spectrometer and 1 m gas cell with polyethylene windows were used).

shows two bands at 3656 and 3624  $\text{cm}^{-1}$ , the latter being more intense, (Fig. 2a). From the variation in the ratio of the integrated intensities of these bands as a function of temperature (from 300 to 453 K) an enthalpy difference of 6.8  $\text{kJ mol}^{-1}$  is derived. For dilute  $\text{CCl}_4$  solutions a doublet is found at 3610 and 3583  $\text{cm}^{-1}$ , (Fig.

2b) and for the pure liquid at 3638 and 3610  $\text{cm}^{-1}$ , (Fig. 1) in the infrared and Raman spectra. In the solid state no  $\nu(\text{OH})$  monomer bands were observed. Monomeric HFTB exhibits only one  $\nu(\text{OH})$  band at 3604  $\text{cm}^{-1}$  in argon matrices, three closely spaced bands at 3586, 3583 and 3579  $\text{cm}^{-1}$  in nitrogen matrices

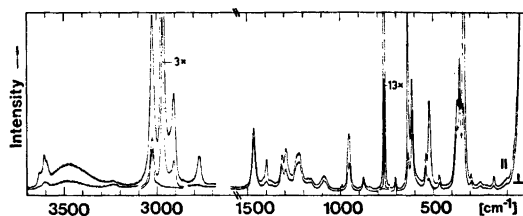


Fig. 1. Raman spectrum of liquid HFTB. Multipass cuvette; 488 nm exciting line; slits 2.5  $\text{cm}^{-1}$ .

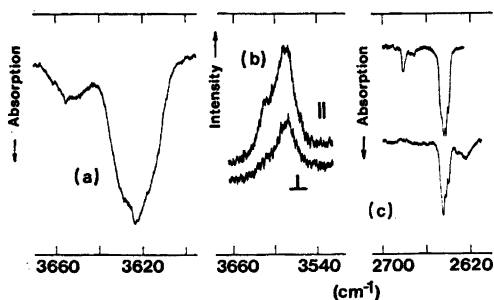


Fig. 2. The  $\nu(\text{OH})$  band of HFTB in several spectra. (a) Infrared vapour spectrum; (b) Raman spectrum of 4% (w/w)  $\text{CCl}_4$  solution; (c) OD alcohol in nitrogen matrices M/A = 1000, 15  $\mu\text{mol}$  deposited. Lower curve is recorded after warming the matrix to 30 K for a few minutes and recooling to 9 K.

and two bands at 3598 and 3590  $\text{cm}^{-1}$  in krypton matrices.

To explain our spectroscopic results in the  $\nu(\text{OH})$  region for HFTB in the vapour and liquid states and in  $\text{CCl}_4$  solution, two conformers, with structures shown in Fig. 3, are proposed. Comparison with the spectra of TFTB<sup>3</sup> (for the  $C_1$  conformer) and of PFTB<sup>4</sup> (for the  $C_s$  conformer) suggest that the higher frequency  $\nu(\text{OH})$  band is due to a conformer having the OH group interacting with only one  $\text{CF}_3$  group (Fig. 3b), while the lower frequency band is due to a conformer stabilized by the interactions of the two  $\text{CF}_3$  groups, (Fig. 3a). The intensity variations of the two  $\nu(\text{OH})$  bands with temperature indicate that the  $C_s$  conformer has a more stable structure than the  $C_1$  conformer in the vapour phase. Assuming that the lower frequency absorption is due to the  $C_s$  conformer in all phases and the higher frequency absorption is due to the  $C_1$  conformer, the  $C_s$  conformer seems to be dominant in the vapour phase and in  $\text{CCl}_4$  solution and the only conformer present in matrices (a frequency

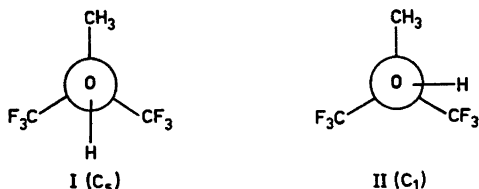


Fig. 3. The conformers of HFTB.

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shift of about 20  $\text{cm}^{-1}$  from vapour phase to argon or krypton matrices is normal for a  $\nu(\text{OH})$  band<sup>5</sup>). Since only one conformer of HFTB seems to be present in matrices, the conversion of the  $C_1$  conformer, apparently present in the vapour phase, must occur either when the molecules strike the matrix during deposition or immediately after deposition.<sup>9,10</sup>

In contrast to HFP<sup>9</sup> and HCP<sup>9</sup> (hexachloro-2-propanol) in dilute nitrogen matrices, where two groups of  $\nu(\text{OH})$  absorptions have been reported, HFTB shows only one such group, most probably due to  $C_s$  conformers. The fine structure of the  $\nu(\text{OH})$  band of HFTB in krypton or nitrogen matrices may be explained in terms of two conformers with structures close to the  $C_s$  conformer (*cf.* Ref. 5). The additional peaks in nitrogen matrix spectra, as indicated by their behaviour on temperature cycling, may arise from different trapping sites (Fig. 2c).

Though HFTB shows only one group of  $\nu(\text{OH})$  bands in dilute nitrogen matrices, two such groups are found for HFTB-OD. The higher frequency bands are at 2681 and 2672  $\text{cm}^{-1}$  and the lower frequency bands at 2648, 2645, 2643 and 2640  $\text{cm}^{-1}$  (Fig. 2c). As the M/A ratio is decreased to about 50, the fine structure disappears and only two bands are found at 2681 and 2645  $\text{cm}^{-1}$ , respectively (Fig. 4a). On warming the matrix, the higher frequency band disappears from the spectra more rapidly than the lower frequency band, while at the same time dimer bands increase in intensity (Figs.

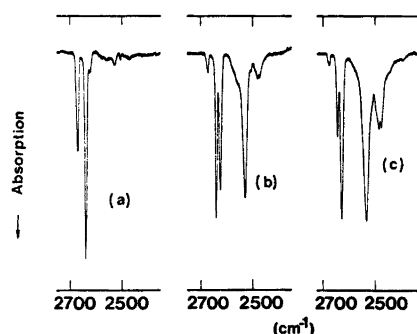


Fig. 4. Association bands of HFTB-OD in nitrogen matrices. (a) M/A = 50, 1  $\mu\text{mol}$  deposited; (b) recorded after warming the (a) matrix to 24 K for 5 min and recooling to 9 K; (c) recorded after warming the (b) matrix to 35 K for 6 min and recooling to 9 K.

2c and 4). Accordingly, it seems likely that HFTB-OD has two conformers in nitrogen matrices. Assuming our conformational assignments for HFTB to be valid also for HFTB-OD in nitrogen matrices, the  $C_1$  conformer seems to associate more readily than the  $C_s$  conformer.

*Molecular vibrations.* The assignments given in Table 1 are based on the infrared frequencies found in dilute matrices, where only the  $C_s$  conformer seems to be present. Since the matrix spectra are very complicated in the region from 1500 to 1000  $\text{cm}^{-1}$ , the assignments should be taken as tentative only.

In very dilute matrices ( $M/A \approx 5000$ ), most of the infrared bands of HFTB do not appear. However, six intense bands are found in the spectra in the region from 1350 to 1050  $\text{cm}^{-1}$ . These undoubtedly involve the six  $\text{CF}_3$  stretching modes (Table 1).<sup>5</sup> The bands at 1365, 1295 and 1076  $\text{cm}^{-1}$  (argon matrix frequencies) are sensitive to diffusion in the matrix and are shifted considerably on OH deuteration. Two of them, assigned to  $\text{CF}_3$  stretching (1295  $\text{cm}^{-1}$ ) and to CO stretching (1076  $\text{cm}^{-1}$ ), in fact arise from mixed vibrations involving the OH bending. The hydroxyl bending bands at 1365 and 897  $\text{cm}^{-1}$  for HFTB and HFTB-OD, respectively, give an isotopic shift ratio of 1.52. This also indicates that some coupling of OH bending with other modes occurs. The frequencies of the monomer  $\delta(\text{OH})$  bands seem to increase from 1328  $\text{cm}^{-1}$  for TB,<sup>1</sup> to 1348  $\text{cm}^{-1}$  for TFTB<sup>3</sup> and to 1382  $\text{cm}^{-1}$  for PFTB<sup>4</sup> (argon matrix frequencies) as the fluorine content of the *tert*-butyl alcohol is increased.

The infrared spectrum of HFTB vapour shows one band at 367  $\text{cm}^{-1}$ , while HFTB-OD shows two bands at 271 and 232  $\text{cm}^{-1}$  due to the hydroxyl torsion. In the latter case, it is tempting to assign the bands to the  $C_s$  and  $C_1$  conformers, respectively. In argon and krypton matrices the  $\tau(\text{OH})$  bands are singlets, with a shoulder on the high-frequency sides. The  $\tau(\text{OD})$  frequency is about 270  $\text{cm}^{-1}$  in both matrices. Three closely spaced  $\tau(\text{OH})$  bands are found for HFTB in nitrogen matrices (Table 1), while HFTB-OD shows only two clearly separated bands at 364 and 318  $\text{cm}^{-1}$  due to the torsion. For HFTB in nitrogen matrices the  $\tau(\text{OH})$  frequencies seem to be about 90  $\text{cm}^{-1}$  higher than the corresponding argon or krypton matrix frequencies (*cf.* Refs. 3 and 8).

In the Raman spectra of liquid HFTB and HFTB-OD, two intense and polarized bands at 766 and 330  $\text{cm}^{-1}$  are assigned to symmetric skeletal stretching and bending bands, respectively. The band at 2770  $\text{cm}^{-1}$  for both liquids is probably due to the overtone  $2\delta(\text{CH}_3)$  in weak Fermi resonance with one of the  $\text{CH}_3$  stretching modes (Fig. 1).<sup>1,3</sup>

A study of the sum and difference bands of the  $\nu(\text{OH})$  band gives the fundamental frequencies of 89  $\text{cm}^{-1}$  for the  $\text{CF}_3$  torsion, 238  $\text{cm}^{-1}$  for a  $\text{CF}_3$  rocking, 330 and 349  $\text{cm}^{-1}$  for CCC bending modes and 367  $\text{cm}^{-1}$  for the hydroxyl torsion, the difference bands being at 3535, 3386, 3294, 3276 and 3258  $\text{cm}^{-1}$  in the infrared spectra of the HFTB vapour, respectively (1 m gas cell and pressures from 20 to 50 mmHg were used). The corresponding sum bands were also detected in the spectra.

For HFTB-OD in nitrogen matrices the bands at 1344, 1216, 1082, 925, 853 and 318  $\text{cm}^{-1}$  show intensity changes parallel to the higher frequency  $\nu(\text{OD})$  band on warming the matrix. These bands are assigned to the  $C_1$  conformer. The fundamental frequencies for the  $C_s$  conformer in nitrogen matrices seem to be almost the same for HFTB and HFTB-OD.

*Association.* HFTB has a lower tendency for association than TFTB<sup>3</sup> or TB,<sup>2</sup> but is certainly more associated than PFTB<sup>4,11</sup> in the liquid state. Hence the degree of association decreases as the fluorine content of the alcohol increases, as is usual for halogenated alcohols.

No association bands were detected for HFTB in the vapour phase. However, HFTB in matrices shows sharp association bands in the  $\nu(\text{OH})$  region. A spectrum of HFTB-OD in nitrogen matrices ( $M/A = 50$ ) is shown in Fig. 4. Two monomer bands at 2681 and 2645  $\text{cm}^{-1}$  are found in the spectrum and practically no association bands appear immediately after deposition (Fig. 4a). After warming the matrix to 25 K and recooling to 9 K the band at 2681  $\text{cm}^{-1}$  decreases in intensity and a tiny feature at 2624  $\text{cm}^{-1}$  on the foot of the 2645  $\text{cm}^{-1}$  band together with a dimer band at 2531  $\text{cm}^{-1}$  increase simultaneously in intensity (the ratio of the peak heights is almost 1:1, Fig. 4b). On further warming the band at 2645  $\text{cm}^{-1}$  decreases in intensity, while the bands at 2624 and 2531  $\text{cm}^{-1}$  become the strongest bands in the region (Fig. 4c). An additional dimer band

Table 2. Infrared frequencies ( $\text{cm}^{-1}$ ) of hydroxyl stretching bands of HFTB and HFTB-OD in several phases.

Species	Vapour	Argon matrix	Nitrogen matrix	Liquid	Solid (196 K)	
$C_1$ conformer	3656	—	—	3632	—	} $\nu(\text{OH})$
$C_s$ conformer	3624	3604	3579	3604	—	
Free OH of associate	—	3590	3555	3591	3582	
Dimer	—	3475	3450	—	—	
Dimer	—	3445	3415	3455	—	
Dimer	—	3375	3335	—	3375	
$C_1$ conformer	2696	—	2681	2683	—	
$C_s$ conformer	2676	2659	2645	2662	—	
Free OD of associate	—	2649	2624	2654	—	
Dimer	—	2575	2553	2575	—	
Dimer	—	2550	2531	—	2507	
Dimer	—	2495	2480	—	2381	

IR frequencies for the  $\nu(\text{OH})$  band of HFTB in dilute  $\text{CCl}_4$  solutions are 3610 ( $C_1$  conformer), 3583 ( $C_s$  conformer) and 3500  $\text{cm}^{-1}$  (dimer).

at 2480  $\text{cm}^{-1}$  appears in the spectrum. The above picture is valid for HFTB and HFTB-OD in all matrices studied, with the exception that two monomer bands are found for HFTB-OD in nitrogen only and that a third, very sharp dimer band with highest frequency of all dimer bands (for HFTB-OD at 2553  $\text{cm}^{-1}$  in nitrogen) appears in the spectra at M/A ratios near 200 (Table 2).

Detection of a separate  $\nu(\text{OH})$  end group absorption at 2624  $\text{cm}^{-1}$  for HFTB-OD in nitrogen suggests open chain (non-cyclic) structures for HFTB dimers. End group bands have been observed also for TFTB<sup>3</sup> and PFTB,<sup>8</sup> while TB<sup>2</sup> does not show such bands in the matrix spectra. Since the dimers of the fluorinated *tert*-butyl alcohols apparently have open-chain structures, there is no reason to believe that TB dimers should have basically different structures (*i.e.* cyclic, *cf.* Ref. 2). Accordingly, the association bands of HFTB in matrices are assigned using the dimer models proposed for TB.<sup>2</sup> The sharp dimer band with the highest frequency (at 2553  $\text{cm}^{-1}$  for HFTB-OD in nitrogen) is assigned to the  $C_s$  dimer, while the two 'main' dimer absorptions (at 2531 and 2480  $\text{cm}^{-1}$  for HFTB-OD in nitrogen) are assigned to  $C_1$  dimers, both proposed models having an open chain structure. It may be mentioned that the dimers of HFTB show more definite structures than those of HFP<sup>5</sup> in matrices.

In the liquid state and solution Raman spectra, an end group band is detected in addition to the monomer  $\nu(\text{OH})$  bands of the  $C_s$  and  $C_1$  conformers (Fig. 1). Since dimers seem to be the only associates of HFTB in matrices, the proportion of dimers must be considerable also in the liquid and solid states, and in solution.<sup>11</sup>

*The origin of the  $\nu(\text{OH})$  end group bands.* Dimer end group bands have not been reported for methanol,<sup>12</sup> ethanol<sup>12</sup> and *tert*-butyl alcohol<sup>2</sup> in matrices, though the dimer concentrations present would have presumed it. Open chain dimer structures have been proposed for all the above-mentioned alcohols in matrices. On the other hand, the existence of the  $\nu(\text{OH})$  end group bands for the fluorinated alcohols TFP (1,1,1-trifluoro-2-propanol),<sup>8</sup> HFP,<sup>5</sup> hexafluoro-2,2-propanediol,<sup>13</sup> TFTB,<sup>3</sup> HFTB (Fig. 4) and PFTB<sup>8</sup> is well established, the bands being shifted to lower frequencies from the monomer  $\nu(\text{OH})$  band as the fluorine content of the alcohol is increased. We propose a non-bonded interaction between the acceptor hydroxyl group and the donor skeleton as the origin of the end group bands of halogenated alcohols. The interaction in question is small for ordinary alcohols.

*Acknowledgements.* The author gratefully acknowledges financial support from the Science Research Council of Finland.

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Received January 12, 1977.