

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

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Infrared spectra of trifluoro-*tert*-butyl alcohol and its OD derivative have been studied in the gaseous and liquid states, in solution, and in argon, krypton and nitrogen matrices. The Raman spectra of the pure liquids and CCl<sub>4</sub> and H<sub>2</sub>O solutions have also been recorded. Only one conformer appears to be present in all phases studied. Assignments of vibrational bands are made. A frequency of 82 cm<sup>-1</sup> is tentatively suggested for the CF<sub>3</sub> torsion. The associates of trifluoro-*tert*-butyl alcohol seem to be mostly dimers in dilute solutions and in dilute matrices.

A few investigations of trifluoromethyl alcohols have been reported in the literature. Barnes *et al.* found a pattern of several satellite bands on either side of the  $\nu(\text{OH})$  band of 2,2,2-trifluoro ethanol (TFE) in the infrared spectrum of the vapour.<sup>1</sup> Vibrational assignments given for TFE<sup>1,2</sup> and 1,1,1-trifluoro-2-propanol (TFP)<sup>3</sup> reveal marked couplings of the fundamental vibrations in the region from 1300 to 900 cm<sup>-1</sup>. Several association studies of trifluoromethyl alcohols in CCl<sub>4</sub> solutions<sup>4-6</sup> and in matrices<sup>1,3</sup> reveal the existence of the  $\nu(\text{OH})$  end group band of a dimer in the spectra and the minor degree of association of the fluoro-alcohols as compared with the corresponding alkanols. Since molecular vibrations<sup>7</sup> and association<sup>8</sup> of *tert*-butyl alcohol (2-methyl-2-propanol, TB) have recently been studied in this laboratory, it was of interest to study the spectra of the corresponding trifluoro alcohol, 2-trifluoromethyl-2-propanol (trifluoro-*tert*-butyl alcohol, TFTB).

## EXPERIMENTAL

TFTB was purchased from Pierce Chemical Co., Rockford, Ill., and purified by fractional distillation.<sup>9</sup> The OD derivative was synthesized simply by shaking the alcohol with D<sub>2</sub>O, collecting the alcohol layer (TFTB 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 on Perkin-Elmer 125, 180 and 621 spectrometers in the wavenumber regions from 5000 to 3000 cm<sup>-1</sup>, from 500 to 50 cm<sup>-1</sup> and from 4000 to 200 cm<sup>-1</sup>, respectively. The wavenumber scales were calibrated using atmospheric water vapour spectra. The usual equipment was used to record the vapour and liquid spectra. The windows of the cells were of CsI or KBr. In the far infrared region, polyethylene windows and a 1 m gas cell were used.

The matrix isolation system used has been described elsewhere.<sup>3</sup> The temperature of the CsI deposition window was kept at about 9 K during the recording of the spectra. During the depositions the temperature was raised to 15 K for argon and to 13 K for nitrogen matrices. Throughout the experiments the deposition rates were about 5 mmol/h of gas mixture. The pressures of the alcohol and the matrix gas were measured with a mercury manometer. The matrix to absorber (M/A) ratio was varied between 2000 and 20.

The Raman spectra were recorded on a Jarrell-Ash 25-305 spectrometer with the 488 nm line of an argon ion laser as the exciting line. During all measurements the spectral slit width was kept constant (at about 2.5 cm<sup>-1</sup>). A multipass cell and 90 degree excitation were used for liquid and solution samples.

The positions of the infrared and Raman bands are believed to be correct to  $\pm 2$  cm<sup>-1</sup>. The frequency differences between sharp peaks were found to be reproducible to 0.5 cm<sup>-1</sup> in

Table 1. The observed infrared and Raman frequencies ( $\text{cm}^{-1}$ ) of  $(\text{CF}_3)(\text{CH}_3)_2\text{COH}$  (fundamental regions).

Vapour	Argon matrix IR <sup>a</sup>	Nitrogen matrix IR <sup>a</sup>	Raman liquid <sup>b</sup>	Fundamental	Tentative Assignments <sup>c</sup>
3647 sh			3621 (2)	} $\nu_1$	$\nu(\text{OH})$ $\nu_1$ , end group
3639 m	3624 m	3617 m	3613 (2)		
3632 sh	3609 sh	3600 sh			
3215 vw			3230 (1)	} $\nu_2$	$\nu_6 + \nu_{35}$ $\nu(\text{CH}_3)$
3013 sh	3012 w	3013 w			
3006 s	3006 w	3006 sh	3003 (30)	} $\nu_3$	$\nu(\text{CH}_3)$
2999 sh		2996 sh			
2992 sh	2992 w	2992 w		} $\nu_4$	$\nu(\text{CH}_3)$
	2964 sh	2968 sh	2959 (as)		
2957 m	2954 w	2956 w	2943 (35)		
	2935 br	2925 br	2923 (as)	} $\nu_5$	$\nu(\text{CH}_3)$
2898 br	2898 sh		2883 (18)		
			2786 (2)	} $\nu_6$	$2\nu_8$ $\nu(\text{CH}_3)$
			2741 (2)		
1485 m	1483 w	1483 w	1464 (6)		
1476 m	1476 vw	1476 sh		} $\nu_8$	$\delta(\text{CH}_3)$
	1471 w	1473 w	1447 (6)		
	1462 sh	1464 sh		} $\nu_{10}$	$\delta(\text{CH}_3)$ $\nu_{20} + \nu_{22}$ $\nu_{24} + \nu_{27}$ $\nu_{18} + \nu_{28}$
	1451 vw	1453 vw			
	1418 vw	1423 vw			
1404 sh				} $\nu_{11}$	$\delta(\text{CH}_3)$
1398 s	1394 m	1396 m	1400 (1)		
1391 sh	1388 vw			} $\nu_{12}$	$\nu_{18} + \nu_{28}$ $\delta(\text{CH}_3)$
	1381 sh	1383 m			
1383 s	1379 m	1382 sh			
	1358 vw	1357 sh		} $\nu_{13}$	$\delta(\text{OH})$
1352 m	1348 m	1355 w			
1341 as		1350 w		} $\nu_{14}$	$\nu_{22} + \nu_{22}$ $\nu_{25} + \nu_{28}$ $\delta(\text{CH}_3)$
	1334 vw	1338 vw			
1327 sh	1328 vw	1332 w	1323 (2)		
1321 s	1319 m	1322 s		} $\nu_{15}$	$\nu_{24} + \nu_{30}$ $\nu(\text{CCC})$
1316 sh	1310 vw	1314 vw			
	1224 w	1224 w	1210 (3)	} $\nu_{16}$	$\nu_{24} + \nu_{32}$ $\nu(\text{CCC})$
	1219 vw	1220 sh			
	1213 w	1215 sh			
	1209 sh	1212 w	1200 (3)	} $\nu_{17}$	$\nu_{24} + \nu_{33}$ $2\nu_{26}$
1199 sh	1199 sh	1201 sh			
1189 vs	1195 vs	1197 s		} $\nu_{18}$	$\nu_{25} + \nu_{30}$ $\nu(\text{CF}_2)$ $\nu_{26} + \nu_{27}$
1182 vs	1192 vs	1191 vs			
	1182 m	1184 s	1170 (1)		
	1173 vs	1173 vs		} $\nu_{19}$	$\nu(\text{CF}_2)$
	1162 m	1165 s			
1150 sh	1149 sh	1149 sh		} $\nu_{20}$	$2\nu_{28}$ $\nu(\text{CF}_2)$ $\nu_{24} + \nu_{36}$
1145 vs	1140 vs	1140 vs	1135 (1)		
	1132 vw	1133 vw			
	1118 vw	1120 sh		} $\nu_{21}$	$\nu(\text{CO})$ $\nu_{24} + \nu_{38}$ $\nu_{25} + \nu_{22}$
1123 sh	1113 sh	1119 vs			
1116 s	1112 vs	1114 m			
	1109 vs	1111 w			
	1102 vw	1108 sh		} $\nu_{22}$	$\nu(\text{CO})$
1011 sh					
1004 w	1000 w	1001 w	1003 (1)	} $\nu_{23}$	$\nu(\text{CO})$ $\nu_{25} + \nu_{28}$ $\nu(\text{CH}_3)$
989 sh	985 sh				
981 s	979 s	982 s	981 (5)		
973 sh		979 m		} $\nu_{23}$	$\nu(\text{CH}_3)$
	940 vw	940 vw	945 (2)		

Table 1. Continued.

881 sh				}	$\nu_{24}$	$\rho(\text{CH}_3)$
875 w	870 w	872 w	872 (11)			
868 sh		870 w		}	$\nu_{25}$	$\nu(\text{CCC})$
764 sh	756 sh		754 (99)			
756 w	753 w	755 w		}	$\nu_{26}$	$\delta(\text{CF}_3)$
749 sh			603 (13)			
608 sh		601 m		}	$\nu_{27}$	$\delta(\text{CF}_3)$
602 s	600 m		584 (8)			
595 sh		582 w		}	$\nu_{28}$	$\delta(\text{CF}_3)$
582 m	581 w	575 w	578 (8)			
575 m	574 w			}	$\nu_{29}$	$\delta(\text{CCO})$
477 sh	468 sh	469 w	476 (1)			
469 m	464 w			}	$\nu_{30}$	$\delta(\text{CCO})$
463 sh		441 w	446 (1)			
444 vw	445 sh			}	$\nu_{31}$	$\delta(\text{CCC})$
439 vw	440 vw	357 m	372 (5)			
358 sh	358 vw			}	$\nu_{32}$	$\delta(\text{CCC})$
351 m	351 w	351 w	357 (8)			
345 sh				}	$\nu_{33}$	$\delta(\text{CCC})$
337 m	339 vw	339 w	341 (9)			
316 sh	307 s	391 m		}	$\nu_{34}$	$\tau(\text{OH})$
		384 sh				
309 s	303 vs	375 s		}	$\nu_{35}$	$\rho(\text{CF}_3)$
302 sh		310 vw				
254 w	260 vw		261 (< 1)	}	$\nu_{36,37}$	$\tau(\text{CH}_3)$
238 w	240 vw	242 vw	241 (1)			
			81 br	}	$\nu_{38}$	$\rho(\text{CF}_3)$
				}	$\nu_{39}$	$\tau(\text{CF}_3)$

<sup>a</sup> Intensities refer to matrices with large M/A ratios. <sup>b</sup> Relative intensities are given in parenthesis. <sup>c</sup> The assignments of combination bands should be understood as informative only. <sup>d</sup> FR refers to Fermi resonance.

the matrix spectra. The non-SI units used are  $1 \text{ \AA} = 10^{-10} \text{ m}$  and  $1 \text{ amu} = 1.660 \times 10^{-27} \text{ kg}$ .

## RESULTS AND DISCUSSION

TFTB has 39 normal modes of vibration, of which three are hydroxyl, 18 methyl, nine trifluoromethyl and nine skeletal modes. All Raman bands should be more or less polarized if we assume  $C_1$  symmetry for the molecule. The most important results and tentative assignments are given in Table 1. Detailed spectroscopic data for the deuterio alcohol (TFTB-OD), including argon and nitrogen matrix spectra, are obtainable from the author on request.

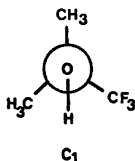


Fig. 1. The conformer of TFTB.

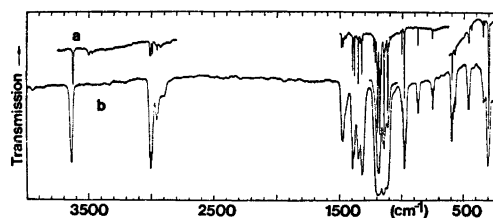


Fig. 2. IR spectra of TFTB. (a) argon matrix, M/A = 2000, 15  $\mu\text{mol}$ ; (b) vapour spectrum, 1 m cuvette with CsI windows, pressures 1.5 and < 0.5 mmHg.

The principal moments of inertia were calculated for the conformer shown in Fig. 1 with the  $\text{CH}_3$  and  $\text{CF}_3$  groups in staggered positions with respect to the carbon skeleton. The following structural parameters were used:  $r(\text{CC}) = 1.537$ ,  $r(\text{CH}) = 1.096$ ,  $r(\text{CF}) = 1.334$ ,  $r(\text{CO}) = 1.427$ ,  $r(\text{OH}) = 0.956 \text{ \AA}$ ;  $\angle(\text{COH}) = 109^\circ$  and all other angles tetrahedral.<sup>10-12</sup> These parameters put the centre of mass almost at the halfway point of the C— $\text{CF}_3$  bond and give principal moments of  $I_A = 196$ ,  $I_B = 274$  and

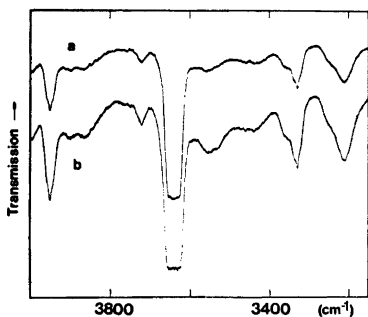


Fig. 3. The OH stretching region in the IR spectrum of TFTB vapour. 1 m gas cuvette with CsI windows, pressures (a) 30 and (b) 52 mmHg.

$I_C = 277 \text{ amu \AA}^2$ . The A-axis of the molecule is very close and almost parallel to the C-CF<sub>3</sub> bond. The molecule is nearly a prolate symmetric top. The band contours in the infrared spectrum of the TFTB vapour, however, are more or less of hybrid type.

**Hydroxyl fundamentals.** Since the spectra of TFTB in vapour, in dilute matrices (Fig. 2) and in dilute solutions show a singlet hydroxyl stretching band, it is likely that the alcohol has only one conformer in these phases. We propose a structure with the hydroxyl group slightly rotated towards the CF<sub>3</sub> group (Fig. 1).

The infrared spectrum of the TFTB vapour shows two bands, which are found to appear symmetrically on both sides of the  $\nu(\text{OH})$  band (Fig. 3). These bands give the sum and difference frequencies of 312 and 308 cm<sup>-1</sup>, respectively. A frequency of 309 cm<sup>-1</sup> is found for the hydroxyl torsion elsewhere in the spectrum. The band at 3720 cm<sup>-1</sup> (Fig. 3) is probably the  $\nu(\text{OH}) + \tau(\text{CF}_3)$  satellite, giving the frequency of 81 cm<sup>-1</sup> for the CF<sub>3</sub> torsion. The corresponding difference band is obviously engulfed by the dimer association band at 3555 cm<sup>-1</sup>.

The  $\nu(\text{OH})$  dimer bands of TFTB are at 3555 cm<sup>-1</sup> in the vapour (Fig. 3), at about 3500 cm<sup>-1</sup> in dilute argon matrices, between 3500 and 3440 cm<sup>-1</sup> in dilute nitrogen matrices (Fig. 4) and at about 3495 cm<sup>-1</sup> in dilute CCl<sub>4</sub> solutions. Polymer bands are seen in the spectra as the concentration of the alcohol is increased. For TFTB in solution and in matrices we propose two groups of associates, dimers and polymers. Additionally, a considerable fraction of 'linear'

dimers seems to be present in matrices, as indicated by the intensities of the separate 'dimer end group' absorptions<sup>13</sup> found in all matrix spectra (Fig. 4).

Several authors have found couplings of the  $\delta(\text{OH})$  vibration of ordinary<sup>7,14</sup> and fluoro-alcohols.<sup>2,3</sup> For TFTB the bands at 1109 and 1348 cm<sup>-1</sup> (argon matrix frequencies) shift considerably on OH deuteration. Both bands behave in a way that is typical of  $\delta(\text{OH})$  bands in matrices. However, the frequency of the former is too low for a pure  $\delta(\text{OH})$  vibration. All matrix spectra show a  $\delta(\text{OD})$  band at about 914 cm<sup>-1</sup> and a new weak band at 1264 cm<sup>-1</sup> for TFTB-OD. The latter band appears more clearly in the Raman spectra of the liquid. Analogous to *tert*-butyl alcohol,<sup>7</sup> it is suggested that a coupling occurs between the  $\delta(\text{OH})$  and  $\nu(\text{CO})$  vibrations for TFTB, as well.

The intense bands at 309 and 303 cm<sup>-1</sup> in the infrared spectra of TFTB in the vapour state and in argon matrices, respectively, (Fig. 2) are assigned to the hydroxyl torsion. The nitrogen matrix frequency of the torsion is about 70 cm<sup>-1</sup> higher than the corresponding argon and krypton matrix frequencies, which seems to be typical of many aliphatic alcohols.<sup>3</sup>

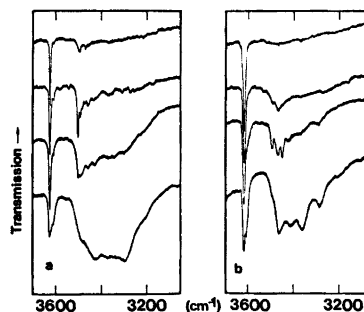


Fig. 4. IR matrix spectra of TFTB in the  $\nu(\text{OH})$  region. Features on the left (a) are reproduced from argon matrix spectra, M/A ratios from top to bottom: 2000 (12  $\mu\text{mol}$ ), 500 (20  $\mu\text{mol}$ ), 200 (70  $\mu\text{mol}$ ) and 50 (28  $\mu\text{mol}$ ). Features on the right (b) are reproduced from nitrogen matrix spectra, M/A ratios from top to bottom: 2000 (25  $\mu\text{mol}$ ), 200 (20  $\mu\text{mol}$ ), 200 (20  $\mu\text{mol}$ ) and 50 (20  $\mu\text{mol}$ ). The third curve from the top on the right is recorded from the M/A=200 matrix after warming the matrix to 30 K for 4 min and cooling back to about 9 K. The numbers in the parentheses indicate the amount of deposited TFTB.

The isotopic shift ratio  $\tau(\text{OH})/\tau(\text{OD})$ , which is 1.25 in the vapour spectrum, 1.21 in argon and 1.32 in nitrogen matrix spectra, is not transferable from argon to nitrogen matrix frequencies or *vice versa*. In the liquid, there is a broad  $\tau(\text{OH})$  association band at  $620\text{ cm}^{-1}$ , which is shifted to  $470\text{ cm}^{-1}$  on OH deuteration.

*Other fundamentals.* The group frequency approximation seems to be satisfactorily valid for TFTB. However, the assignments given in Table 1 should be taken as tentative only.

In the Raman spectra of liquid TFTB the two bands at  $2786$  and  $2741\text{ cm}^{-1}$  are most probably the overtones of the  $\text{CH}_3$  deformations. Since these bands are on the lower frequency side of the methyl stretching bands, a slight Fermi interaction may occur between the overtones and the stretchings.<sup>15</sup> The feature at  $260\text{ cm}^{-1}$  in the Raman spectrum of liquid TFTB is assigned to the methyl torsions. *tert*-Butyl alcohol shows a similar type of band at about  $270\text{ cm}^{-1}$ , which is shifted to  $190\text{ cm}^{-1}$  in the spectrum of the corresponding  $\text{CH}_3$  deuterated alcohol.<sup>7</sup>

The bands, assigned to  $\text{CF}_3$  stretching, appear with very low intensity in the Raman spectra but are very strong in the infrared (Fig. 2). The bands at about  $600$ ,  $582$  and  $575\text{ cm}^{-1}$ , which are not present in the spectra of *tert*-butyl alcohol and are well separated from other vibrational bands of TFTB, are assigned to the  $\text{CF}_3$  deformations.

The frequency of the broad shoulder at  $81\text{ cm}^{-1}$  in the Raman spectrum of the liquid is suitable for the  $\text{CF}_3$  torsion. To obtain further support for this assignment, far infrared spectra of TFTB vapour were recorded. In spite of some instrumental difficulties, evidence of a broad band at about  $85\text{ cm}^{-1}$  was obtained. Since a value of  $81\text{ cm}^{-1}$  was obtained from one of the  $\nu(\text{OH})$  sum bands (for the fundamental frequency), it is likely that the  $\text{CF}_3$  torsion frequency of TFTB is about  $82\text{ cm}^{-1}$ . The value is markedly larger than has been reported for  $\text{CF}_3\text{COCl}$ <sup>16</sup> ( $45\text{ cm}^{-1}$ ) and for  $\text{CF}_3\text{CHO}$ <sup>17</sup> ( $55\text{ cm}^{-1}$ ), markedly smaller than that for  $\text{CF}_3\text{CH}_2\text{OH}$ <sup>1</sup> ( $120\text{ cm}^{-1}$ ), but of the same order of magnitude as those given for  $\text{CF}_3\text{CHOHCH}_3$ <sup>3</sup> ( $75\text{ cm}^{-1}$ ) and  $(\text{CF}_3)_3\text{COH}$ <sup>18</sup> ( $70\text{ cm}^{-1}$ ).

The coupling of the CO stretching mode has been discussed above. The strongest Raman band of TFTB at  $755\text{ cm}^{-1}$  is assigned to the symmetrical CCC stretching mode. The strong Raman band at  $339\text{ cm}^{-1}$  is probably due to the symmetric CCC bending vibration.

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