Spectrochimica Acta, Vol. 35A, pp. 585 to 592
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0584-8539/79/0601-0583$02.00/0

Vibrational spectra and normal coordinate analysis of 2,2,2-trichloroethanol and 2,2,2-trifluoroethanol

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(*Received* 3 *January* 1978)

Abstract—The vibrational spectra of 2,2,2-trichloroethanol and 2,2,2-trichloroethanol and their OD deuterated analogues have been studied in argon, nitrogen and mixed argon–nitrogen matrices. The matrix spectra of the CD_2 deuterated and totally deuterated trifluoroethanol and the Raman and i.r. spectra of the liquid alcohols have also been recorded. A vibrational assignment, supported by normal coordinate analysis, is proposed for both alcohols.

INTRODUCTION

We have reported elsewhere the results of matrix i.r. studies on the halogenated ethanols FCH_2CH_2OH (FE) [1], $ClCH_2CH_2OH$ (CE) [2], F_2CHCH_2OH (DFE) and Cl_2CHCH_2OH (DCE) [3]. We now complete the series with a study of the matrix i.r. spectra of the trihalogenated ethanols F_3CCH_2OH (TFE) and Cl_3CCH_2OH (TCE). The few data published on TCE [4–6] are related only to the liquid state. To our knowledge, no vibrational assignment has been reported. The i.r. spectra of TFE have been studied by Barnes *et al.* [7] both in the vapour state and in argon matrix. Although their emphasis is on the OH stretching region, they also suggest a vibrational assignment. No normal coordinate analysis has been reported.

Considering the rotation about the C—O bond, the 2,2,2-trihaloethanols have two stable conformers (Fig. 1). It has been noted previously [4, 7] that in the liquid state most haloethanols exhibit a single strong OH stretching band, with a slight asymmetry on the high-wavenumber side. As the *α-trans* effect [8] should increase the νOH wavenumber of the *trans* species, the higher wavenumber peak has been assigned to the *trans* and the lower to the *gauche* conformer. Energetically this effect should also favour the formation of the *trans* conformer, but in most haloethanols the *gauche* component is found to prevail. A possible explanation is that the intramolecular OH——X (X = halogen) interaction stabilizes the *gauche* conformer (see eg [9]).

In FE and CE, i.r. irradiation induces interconversion from the *gauche* to the *trans* conformer [1, 2].

EXPERIMENTAL

2,2,2-Trichloroethanol and 2,2,2-trifluoroethanol (E. Merck AG) were used as received. TCE-OD and TFE-OD were prepared by adding D_2O to the alcohols and then removing water by distillation under normal pressure and the use of molecular sieves. The drying was continued until the amount H_2O, HDO and D_2O remaining, as determined from the i.r. spectra, was considered small enough (under about 10%). TFE-CD_2OD (E. Merck AG) was used without further purification. TFE-CD_2OH was obtained by repeated adding of H_2O to the trideuterated alcohol and then distilling off the alcohol.

The i.r. matrix spectra were recorded in argon, nitrogen and mixed argon–nitrogen media as previously described [10]. The deposition temperature was in most cases about 14 K and the matrix to absorber (M/A) ratio was varied between 50 and 2000. The i.r. spectra of the liquid alcohols were also recorded and are occasionally referred to in the text. The Raman spectra of the liquids, including polarization measurements were recorded with a Jarrell-Ash 25-305 spectrometer and argon ion laser (488 nm exciting line). A slit servo system was used to keep the spectral slit width constant at 2.5 cm^{-1}. The positions of the i.r. and Raman lines are believed to be accurate to within ± 2 cm^{-1} (± 1 cm^{-1} in the matrix spectra).

NORMAL COORDINATE ANALYSIS

The programmes of Schachtschneider and Snyder [11] were used to construct the Wilson G matrix and the Urey–Bradley Z matrix. The following molecular parameters were employed [12]: $r(C—C) = 1.54$ Å, $r(CO) = 1.33$ Å, $r(O—H) = 0.96$ Å, $r(C—H) = 1.09$ Å, $r(C—F) = 1.39$ Å, $r(C—Cl) = 1.77$ Å, $<COH = 106°$ and all other angles tetrahedral (*gauche* conformer). Figure 1 gives the internal coordinates. The local symmetry coordinates of Table 1 were used to facilitate the interpretation of the potential energy distributions. The normal coordinate calculations were carried out with a programme written by the author. Twenty-three Urey–Bradley potential parameters were adjusted to give a satisfactory fit with the observed fundamentals of the argon spectra of TCE and TFE. Initial force fields were constructed with the aid of corresponding potential parameters of DCE and DFE [3]. The resulting force constants are listed in Table 2.

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Figure 2 shows the i.r. spectrum of TCE in argon matrix. The observed wavenumbers are listed in Table 3, and the observed and calculated fundamentals of

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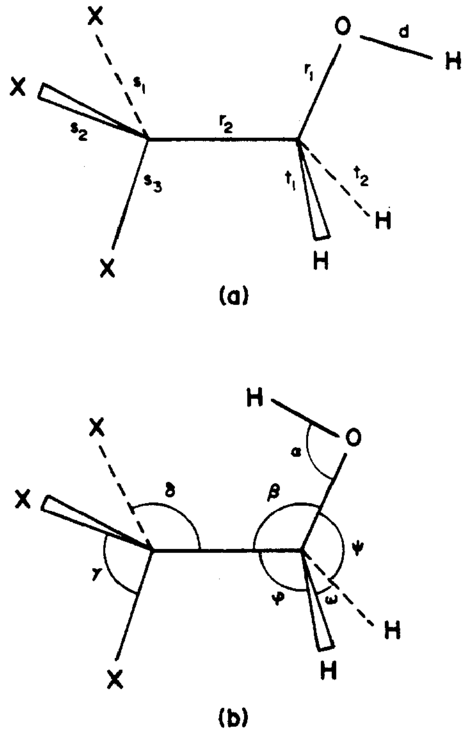

Fig. 1. The conformers and internal coordinates of 2,2,2-trihaloethanols. (a) *trans*, (b) *gauche* conformer.

Table 1. The local symmetry coordinates for TCE and TFE

$S_1 = d$
$S_2 = r_1$
$S_3 = r_2$
$S_4 = 1/\sqrt{3}(s_1 + s_2 + s_3)$
$S_5 = 1/\sqrt{6}(2s_1 - s_2 - s_3)$
$S_6 = 1/\sqrt{2}(t_1 + t_2)$
$S_7 = \alpha$
$S_8 = 1/2(\varphi_1 + \varphi_2 - \psi_1 - \psi_2)$
$S_9 = 1/2\sqrt{5}(4\omega - \varphi_1 - \varphi_2 - \psi_1 - \psi_2)$
$S_{10} = 1/\sqrt{30}(5\beta - \varphi_1 - \varphi_2 - \psi_1 - \psi_2 - \omega)$
$S_{11} = 1/\sqrt{6}(\delta_1 + \delta_2 + \delta_3 - \gamma_1 - \gamma_2 - \gamma_3)$
$S_{12} = 1/\sqrt{6}(2\delta_1 - \delta_2 - \delta_3)$
$S_{13} = 1/\sqrt{6}(2\gamma_1 - \gamma_2 - \gamma_3)$
$S_{14} = 1/\sqrt{2}(s_1 - s_2)$
$S_{15} = 1/\sqrt{2}(t_1 - t_2)$
$S_{16} = 1/2(\varphi_1 - \varphi_2 - \psi_1 + \psi_2)$
$S_{17} = 1/2(\varphi_1 - \varphi_2 + \psi_1 - \psi_2)$
$S_{18} = 1/\sqrt{2}(\delta_1 - \delta_2)$
$S_{19} = 1/\sqrt{2}(\gamma_1 - \gamma_2)$
$S_{20} = \tau(CX_3)$
$S_{21} = \tau(OH)$
$S_{22} = 1/\sqrt{6}(\beta + \omega + \varphi_1 + \varphi_2 + \psi_1 + \psi_2)$ (red.)
$S_{23} = 1/\sqrt{6}(\delta_1 + \delta_2 + \delta_3 + \gamma_1 + \gamma_2 + \gamma_3)$ (red.)

both TCE and TCE-OD, together with the potential energy distribution for TCE, are listed in Table 4.

Hydroxyl vibrations

Table 2. The Urey–Bradley potential parameters for TCE and TFE

	TCE	TFE
K(OH)	7.0913 mdyn/Å	7.1650 mdyn/Å
K(CO)	3.2531	3.4165
K(CC)	3.2094	3.9695
K(CX) (X=halogen)	1.9425	3.6704
K(CH)	4.0794	4.2109
H(COH)	0.4084 mdynÅ	0.4897 mdynÅ
H(CCO)	0.6341	0.6481
H(CCX)	0.3997	0.6114
H(XCX)	0.6449	1.0209
H(CCH)	0.6041	0.5395
H(OCH)	0.3977	0.3720
H(HCH)	0.4024	0.4383
$\gamma(CX_3)$	0.0606	0.0582
$\gamma(OH)$	0.0431	0.0401
$F(C_1 - H_1)$	0.5488 mdyn/Å	0.5615 mdyn/Å
$F(C_1 - X)$	0.2071	0.3328
$F(X - X)$	1.3301	1.2545
$F(C_2 - O)$	0.9543	0.9405
$F(C_2 - H_{2,3})$	0.3454	0.4536.
$F(O - H_{2,3})$	0.8446	0.8750
$F(H_2 - H_3)$	0.1172	0.0221
$\chi(OCH_2)$	0.4943 mdynÅ	0.5184 mdynÅ
$\chi(CX_3)$	0.0748	0.0751

In the argon medium the OH stretching band is a sharp doublet (peaks at 3620 and 3615 cm^{-1}). In contrast to the earlier results for haloethanols [1–4], the higher wavenumber peak corresponding to the *trans* compound is slightly more intense than the lower wavenumber *gauche* peak. No changes in the relative intensities were found during the i.r. irradiation of the matrix in the time range 30 s to 24 h. When the matrix is warmed, the intensity ratio is constant up to about 22 K, after which the lower wavenumber peak begins to lose intensity irreversibly. In the nitrogen matrix spectra the νOH band is at 3617 cm^{-1} and has a slight shoulder on the lower wavenumber side. This asymmetry disappears irreversibly when the matrix is warmed to about 32 K. The prevalency of the *gauche* conformer in most haloethanols is usually explained by interaction between the halogen atom and the hydrogen atom of the OH group [1–4, 13]. In ethanol itself, however, the *trans* form is favoured because of the participation of the oxygen lone pair orbital in the antibonding σ C—H orbital in trans position on an adjacent carbon atom [8, 14]. In TCE this *trans* lone pair interaction is evidently strong enough to make the *trans* conformer about as stable as the *gauche* conformer.

The strong OH torsion peak behaves similarly to the νOH peak. In argon medium the torsion band displays a small peak on the lower wavenumber side, and in nitrogen medium the smaller peak occurs as only a weak shoulder. The wavenumber of the OH torsion band is 96 cm^{-1} lower in the argon than in the nitrogen matrix. This shift is much larger than the shifts observed for CE and DCE [2, 3], but still considerably smaller than for FE and DFE [1, 3]. Correspondingly, the

Table 3. The observed i.r. and R wavenumbers for TCE

Argon matrix	Nitrogen matrix	Raman[†] (liquid)	Fundamental	Approximate description
3620 m	3617 s	3590(6)P 0.2	ν_1	νOH
3615 m	3610 sh			
3517				νOH (end group)
3565				
3540				νOH (assoc., dimer)
3515				
3483				
3468				
3350 br		3400(8)br		νOH (polymer)
2942 vw	2964 vvw	2972(30)DP 0.57	ν_2	νCH
2925 vw	2942 vw	2937(56)P 0.09	ν_3	νCH
2872 vvw	2878 vvw	2870(14)P 0.08		$2\cdot\nu_4$(FR with ν_3)
1459 vvw	1451 vw	1446(19)DP 0.75	ν_4	δCH
1452 w				
1398 vw			ν_5	δCH
1392 vvw				
1379 m	1381 m	1377(1)P 0.50	ν_6	δCH
1354 vw	1354 vw			δCH (trans)
1350 sh	1351 vvw			δCH (trans)
1220 sh		1241(3)DP 0.56		assoc. band ν_7
1213 s	1221 m		ν_7	δCOH
1211 s				
1104 vs	1104 vs	1097(8) P 0.35	ν_8	νCO
1096 vs	1100 m			
1037 w	1037 w	1032(11)DP 0.68	ν_9	νCC
1003 vs	1009 vs	1012(5)DP 0.64	ν_{10}	δCH
849 vw	850 w			$(\nu_{17} + \nu_{13})$
839 vw	840 vw			$(2\cdot\nu_{14})$
831 sh	821 vs	816(18)P 0.28	ν_{11}	νCCl
827 sh				
822 vs				
819 sh				
721 s	723 vs	715(26)DP 0.75	ν_{12}	νCCl
719 s				
567 m	568 m	567(91)P 0.07	ν_{13}	νCCl
421 vw	421 vvw	428(100)P 0.06	ν_{14}	δCO
	416 vvw			
353 s	353 m	340(20)P 0.40	ν_{15}	δCCl
322 w	326 m	328(28)P 0.28	ν_{16}	δCCl
319 w	319 sh			
296 vvs	388 m	372(4)P	ν_{17}	τOH
276 vvw	372 sh			
261 vvw		268(42)P 0.40	ν_{18}	δCCl
246 w		250(42)P 0.42	ν_{19}	δCCl
		188(23)P 0.30	ν20	δCCl

* Infrared intensities refer to matrix spectra of large M/A values.

† Relative intensities in parentheses. P = polarized, DP = depolarized.

wavenumber of the OH stretching band of TCE is only 3 cm^{-1} higher in argon than in nitrogen (see Table 7).

The degree of self-association of TCE is very low even in matrices of low M/A ratio. This is in accordance with the general trend in the sequence ethanol, CE, DCE and TCE. CONNOR and REID have found a limited correlation between the OH proton resonance shift and the integrated intensity of the free OH stretching band in this sequence [15]. However, warming the

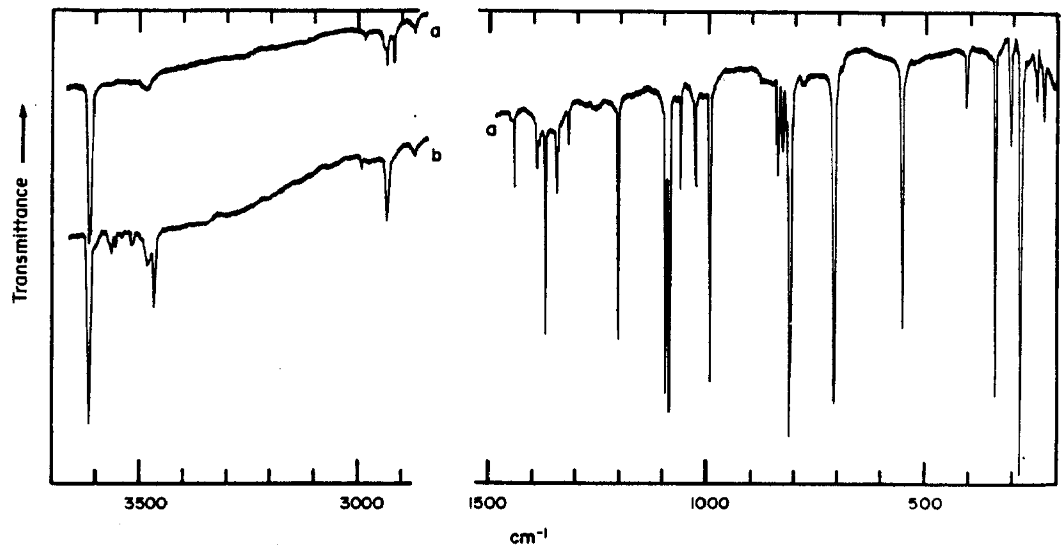

Fig. 2. Argon matrix spectrum of TCE. M/A = 200, (a) recorded at 11 K, (b) matrix warmed to 36 K, cooled, and recorded at 11 K

Table 4. The observed and calculated fundamentals of TCE and TCE–OD. PED of TCE (co-ordinate number in parentheses).

TCE		TCE-OD		PED	Assignment
ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}		
3620	3620	2673	2632	100(1)	νOH
2942	2942	2942	2942	100(15)	νCH_2 "asym."
2925	2925	2925	2926	99(6)	νCH_2 "sym."
1452	1453	1452	1452	86(8) + 7(3)	δCH_2 bend
1398	1401	1398	1401	97(16)	δCH_2 bend
1379	1377	1373	1375	95(9)	δCH_2 sciss.
1213	1212	886	922	86(7) + 5(3)	δCOH
1100	1109	1100	1117	45(3) + 42(2)	νCC + νCO
1037	1027	1037	1035	47(2) + 27(3) + 6(11)	νCO + νCC
1003	984	1003	984	75(17) + 12(14)	δCH_2 rocking
822	818	822	800	56(5) + 23(13) + 12(10)	$\nu ClCCl_2$ "sym."
720	721	718	721	62(14) + 24(19) + 8(17)	νCCl_2 "asym."
567	551	563	548	88(4)	νCCl_3 "sym."
421	436	419	419	52(10) + 19(11) + 23(5)	δCCO
353	369	353	369	90(19) + 7(14)	δCCl_3 bend
322	363	322	362	90(13)	δCCl_3 bend
296	292	221	238	93(21)	τOH
261	264	263	261	67(11) + 15(4) + 6(12)	δCCl_3 bend
246	210	246	194	92(18)	δCCl_2 rocking
-	144	-	142	74(12) + 15(10)	δCCl_3 rocking
-	42	-	40	93(20)	τCCl_3

matrices of low M/A ratio produces some association structure in the νOH region (see Fig. 2), similar to that of DCE but much weaker than that of CE.

Spectra of TCE were also recorded in mixed argon–nitrogen matrices. The splitting of the OH stretching band in argon disappears when even a small amount (about 1 %) of nitrogen is added to argon, and the peak appears at 3617 cm^{-1}. The effect of adding nitrogen is more clearly seen in the OH torsion region, where the very intense bands of the τOH and an δCCl mode (at 296 and 353 cm^{-1}, resp.) lose intensity considerably. The band of the OH torsion mode of the nitrogen complex at 392 cm^{-1} appears only at high nitrogen contents.

The i.r. spectrum of liquid TCE exhibits a broad νOH association band centered at 3380 cm^{-1}, and two smaller peaks at 3660 and 3575 cm^{-1} which are obviously due to the monomer and dimer forms, respectively. The OH torsion band in liquid state is weak and broad, centered at about 600 cm^{-1}.

Table 5. The observed i.r. and R wavenumbers for TFE[*]

Argon matrix	Nitrogen matrix	Raman[†] (liquid)	Fundamental	Approximate description
3639 m 3625 sh	3637 sh 3629 m	3638(5)P 0.2	ν_1	νOH
3540				νOH (end group)
3510		3380(8) br		νOH (assoc.,dim.)
3004 vvw	3002 vvw	2999(15)DP 0.70	ν_2	νCH
2952 vw	2952 vw	2968(72)P 0.10	ν_3	νCH
2892 vvw	2894 vvw	2893(13)P 0.07		$2\cdot\nu_4$ (FR with ν_3)
1454 w	1455 vw	1455(17)DP 0.71	ν_4	δCH
1421 w 1408 w	1422 vw 1415 vw		ν_5	δCH
1370 m 1366 w 1358 vw 1355 vw	1383 vvw 1380 vw 1372 w	1380(1)	ν_6	δCH
1302 vvw	1313 vvw			$\nu_{14} + \nu_{15}$
1300 sh		1282(9)P 0.55		assoc. band
1288 vs	1286 vs		ν_7	δCOH
1276 sh				assoc. band
1262 vs	1266 vs		ν_8	νCC
1184 sh				assoc. band
1172 vvs	1174 vvs 1165 vs	1169(6)DP 0.60	ν_9	νCF
1140 s 1137 vs	1141 vs 1137 m	1151(8)DP 0.62	ν_{10}	νCF
1103 br	1097 br			assoc. band
1085 vs 1081 w	1090 vs	1101(16)P 0.14	ν_{11}	νCO
941 ms 936 m 934 m	946 ms 940 m 937 w	947(6)DP 0.70	ν_{12}	δCH
836 w 830 m	830 w 828 w	829(100)P 0.02	ν_{13}	νCF
667 m 662 m 657 vw	664 s 660 vw	665(15)P 0.55	$\nu_{14,15}$	δCF
545 w	546 w	547(24)P 0.19	ν_{16}	δCF
415 vw	417 vw	422(22)P 0.23	ν_{17}	δCO
365 w 359 w	320 vvw 336 vw	359(6)P 0.10	ν_{18}	δCF
277 s 270 vs	413 m 408 m		ν_{19}	τOH
220 w		237(1)	ν_{20}	δCF
		60(1)	ν_{21}	τCF

[*] Infrared intensities refer to matrix spectra of large M/A values.

[†] Relative intensities in parentheses. P = polarized, DP = depolarized.

Other fundamentals

In argon spectra of TCE many of the fundamentals are split into two adjacent peaks. These pairs behave similarly to the OH stretching and torsion bands when the matrices are warmed: in each case the lower wavenumber component either loses intensity or disappears altogether. However, i.r. irradiation of the matrices does not cause any change in the relative intensities of the peaks, so that a definite assignment to *trans* or *gauche* conformer cannot be made.

The assignment of the bands in the region 1200–800 cm^{-1} is somewhat arbitrary because of the mixing of

Table 6. The observed and calculated fundamentals of TFE, TFE–CH_2OD, TFE–CD_2 and TFE–CD_2OD. PED of TFE (coordinate number in parenthesis)

TFE		TFE-CH_2OD		TFE-CD_2OH		TFE-CD_2OD		PED	Assignment
ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}	ν_{obs}	ν_{calc}		
3639	3639	2686	2646	3639	3639	2687	2647	100(1)	νOH
3004	3004	3004	3004	2189	2217	2189	2217	100(15)	νCH_2 "asym."
2952	2952	2952	2953	2144	2139	2144	2139	99(6)	νCH_2 "sym."
1454	1462	1456	1459	1136	1115	1138	1115	75(8) + 14(3)	δCH_2 bend
1408	1418	1417	1418	1076	976	1084	976	89(16) + 7(14)	δCH_2 bend
1366	1364	1314	1358	979	969	979	990	81(9) + 8(7)	δCH_2 sciss.
1288	1300	1283	1269	1346	1349	1348	1333	44(7) + 22(3) + 11(9)	δCOH + νCC
1262	1240	1015	963	1323	1262	-	927	40(3) + 28(7) + 14(11) + 11(4)	νCC + δCOH
1172	1161	1202	1161	1211	1201	1211	1201	51(14) + 22(19) + 14(17)	νCF_2 "asym"
1137	1151	1137	1161	1190	1173	1190	1182	59(5) + 25(13)	νFCF_2 "sym"
1085	1087	1097	1087	1077	1010	1085	1022	81(2)	νCO
936	906	936	906	770	765	770	765	71(17) + 18(14)	δCH_2 rocking
830	826	829	822	816	818	802	816	91(4)	νCF_3 "sym."
662	648	660	648	651	647	644	647	78(13) + 19(5)	δCF_3 bend
662	646	-	646	-	646	-	646	82(19) + 16(14)	δCF_3 bend
545	569	544	553	532	547	532	533	50(11) + 28(10) + 9(3)	δCF_3 + δCCO
415	402	410	393	410	396	406	388	32(11) + 28(12) + 23(10)	δCCO + δCF_3
365	346	360	344	331	314	326	312	86(18) + 7(21)	δCF_2 rocking
270	272	239	227	269	272	239	226	92(21) + 8(18)	τOH
220	232	220	206	216	231	216	201	54(12) + 37(10)	δCF_3 rocking
-	47	-	45	-	44	-	42	95(20)	τCF_3

Table 7. The wavenumbers (cm^{-1}) of the τOH and νOH bands in argon and nitrogen matrices for some haloethanols

	τOH			νOH		
	Ar	N_2	shift	Ar	N_2	shift
CE [2]	329	363	+24	3614	3624	+10
DCE [3]	320	368	+48	3622	3630	+8
TCE	296	388	+92	3620	3617	-3
FE [1]	284	407	+123	3644	3636	-8
DFE [3]	296	413	+117	3643	3632	-11
TFE	270	408	+138	3639	3629	-10

the fundamentals. This can be seen by examining the PEDs of the normal modes of this region. The COH bending band, however, was clearly identified by OD deuteration, and by its association band, even though the association tendency of TCE is weak.

The three strong bands at 822, 720 and 567 cm^{-1} (argon spectrum) are assigned to the CCl stretchings, in accordance with several papers dealing with molecules that contain CCl_3 groups (see eg. [5, 16–18]).

The bands for the CCl_3 torsion and one of the rocking modes were not found in the region over 200 cm^{-1} and thus were not used in the least squares refinement of the force constants. The same force constant as for DCE was used in estimating the CCl_3 torsion wavenumber.

The deuteration of the OH group affects only slightly the spectra of TCE (except for the hydroxyl vibrations). In argon matrix spectrum the fundamentals of TCE–OD are split like those of TCE.

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Figure 3 shows the i.r. spectrum of TFE in argon medium. The observed wavenumbers are listed in Table 5, and the observed and calculated fundamentals for TFE, TFE–OD, TFE–CD_2OH and TFE–CD_2OD are listed in Table 6, together with the potential energy distribution for TFE.

Hydroxyl vibrations

The OH stretching and torsion bands are at 3639 and 270 cm^{-1}, respectively. The stretching band shows no conformational splitting or asymmetry, but the torsion band has a shoulder at about 277 cm^{-1}. The relative intensities of the shoulder and the main band do not change during the irradiation of the matrices, however, and warming the argon matrices has no effect on this shoulder. The association structure produced in the spectra by warming the matrices shows TFE to be about as little associative as TCE (see Fig. 3). This is in accordance with the above-mentioned lack of splitting of the νOH peak. In TFE the interaction between the hydrogen in the OH group and the CF_3 fluorine atoms is apparently so strong that the molecule exists almost totally in *gauche* form. This strong intramolecular influence also makes the molecule less capable of forming a hydrogen bond with other TFE molecules.

In nitrogen medium the OH stretching band at 3629 cm^{-1} shows distinct shoulders at 3632 and 3639 cm^{-1}. Upon warming, the shoulder at 3639 cm^{-1} disappears irreversibly, but that at 3632 cm^{-1} remains unchanged.

Warming the nitrogen matrix causes interesting changes in the OH torsion region, which consists of

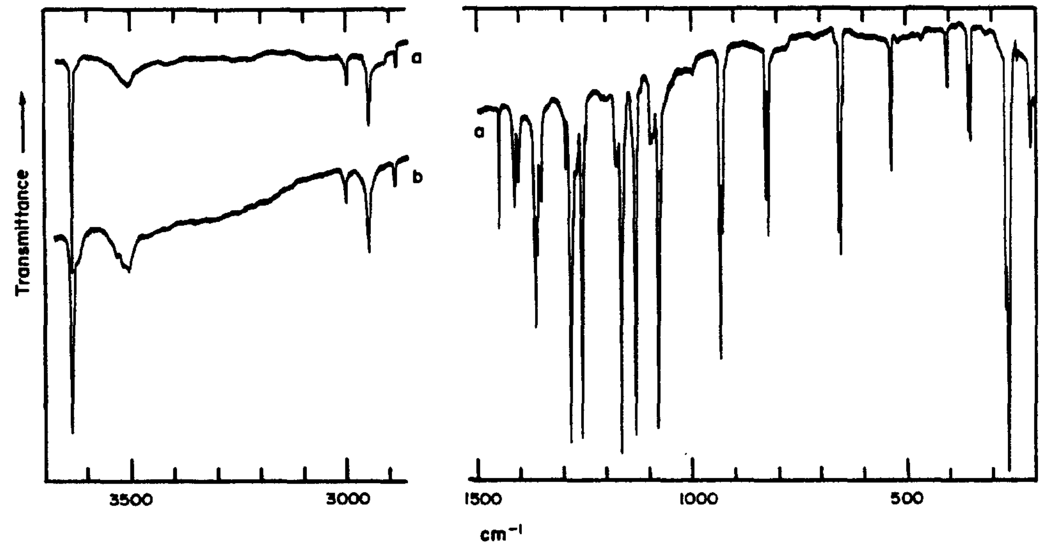

Fig. 3. Argon matrix spectrum of TFE. M/A = 200, (a) recorded at 11 K, (b) matrix warmed to 36 K, cooled, and recorded at 11 K.

several adjacent peaks (see Fig. 4). The most prominent peaks are at 417, 413 and 408 cm^{-1}. When the matrix is warmed over 16 K, the peak at 413 cm^{-1} begins to lose intensity and the peak at 408 cm^{-1} gains intensity, both *reversibly* (Fig. 4). The 417 cm^{-1} peak remains unchanged. In the region 330–300 cm^{-1} both reversible and irreversible changes can be seen.

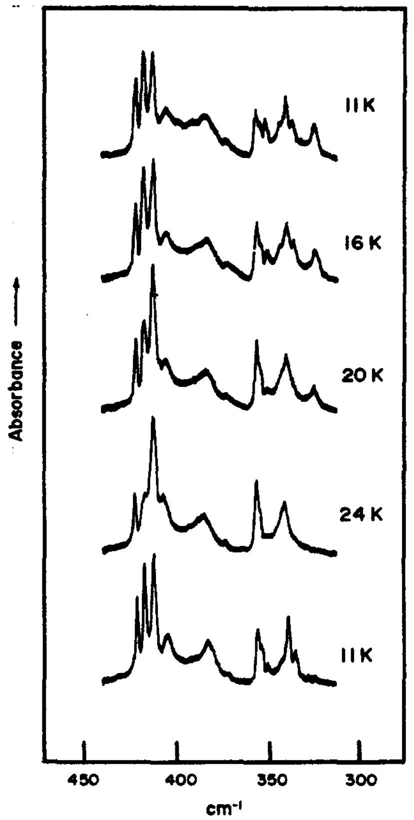

Fig. 4. Reversible temperature changes in the OH torsion region of TFE in N_2 matrix. M/A = 1000.

In order to get more information on the τOH band, the i.r. spectra of TFE were also recorded in mixed argon-nitrogen matrices. The intensity of the τOH peak in argon (at 270 cm^{-1}) diminishes rapidly even at low nitrogen contents, and disappears totally when the nitrogen content exceeds about 6%. Simultaneously, two new peaks appear in the region 330–300 cm^{-1}. These cannot be assigned to the τOH vibration of the nitrogen complex because the wavenumber of the OH stretching vibration is 10 cm^{-1} lower in nitrogen than in argon, which indicates that the corresponding shift of the τOH vibration should be of the same order of magnitude as for FE and DFE (cf. Table 7). Thus the peaks in the region 330–300 cm^{-1} are assigned to CF_3 bending modes of the nitrogen complex. When the nitrogen content is increased still more, new peaks appear at 413 and 408 cm^{-1}, while the CO bending mode, at 415 cm^{-1} in the argon spectrum, shifts to 417 cm^{-1}.

The reversible temperature effects in the τOH region can probably be related to multiple trapping sites in the nitrogen matrix, as no corresponding changes were noted in the νOH region. BARNES and WHITTLE [19] discuss reversible temperature effects in terms of interconversion of conformers.

The deuteration of the CH_2 group does not seem to affect the νOH and τOH vibrations, which are found, respectively, to have the same wavenumbers within 1 cm^{-1}. The OD stretching and torsion vibrations are similarly unaffected by the deuteration of the CH_2 group.

Other fundamentals

The vibrational assignment for TFE is in good agreement with that published by BARNES *et al.* [7], except that we did not find a CH_2 rocking band at 786 cm^{-1} in the argon matrix. Instead, a band at 936 cm^{-1} was assigned to the ρCH_2 mode, and the bands at 1137 and 1085 cm^{-1} to νC and νCO vibrations, as indicated by normal coordinate calculations. The spectrum of TFE–OD differs very little from that of TFE, and thus its assignment is largely based on normal coordinate results. In both cases the bands in the region 1250–1000 cm^{-1} represent strongly mixed modes. This can be seen from the PEDs of the normal modes, and even from the spectra. For example, the OH bending band, which is often easily identified by its association behaviour, was here difficult to assign because the bands at 1262, 1172, 1137 and 1085 cm^{-1} all exhibit an M/A dependent association band.

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