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The Vibrational Spectra of 1,1,2-Tribromoethane

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The infrared spectrum of 1,1,2-tribromoethane was studied in the region from 4000 to 200 cm^{-1} as a liquid, in various solvents, and as a solid at −160°. Raman spectral data were recorded and semiquantitative polarization data obtained, using helium-neon laser excitation.

The molecule exists as a mixture of rotational conformers in the liquid state and in solution, but only one form is present in the crystal. A considerable displacement of the conformational equilibrium with solvent dielectric constant was observed by means of infrared as well as Raman spectroscopic methods. The less polar conformer (C_1 symmetry) is present in the crystal. Tentative assignments of the fundamental frequencies are presented.

The equilibrium between the staggered conformers of halogenated ethanes has been studied in great detail and the work has been reviewed in three monographs [1–3] and several review articles. Among the ethanes particularly the 1,2-dihalo- and the 1,1,2,2-tetrahaloethanes have been extensively investigated by various methods. The high symmetry of these molecules generally leads to an unambiguous interpretation of the vibrational spectra and reveals a mixture of *trans* (C_{2h}) and *gauche* (C_2) conformers in the vapour and the liquid states, with only the *trans* present in the crystal.[4]

Some work has also been done on the 1,1,2-trihaloethanes. In the trichloroethane the conformational equilibrium has been studied by infrared [5,6] and Raman [7] spectroscopy and dipole,[8] thermodyamic,[9] ultrasonic,[10] and proton magnetic resonance [11] measurements. The corresponding 1,1,2-tribromoethane has also been studied to some extent.[5,8,10] However, since the infrared [5] and Raman [12] studies of this molecule were reported a long time ago, we felt it would be of interest to make a more complete study in an extended frequency range and with a much higher resolution.

EXPERIMENTAL

The sample of 1,1,2-tribromoethane had previously been used for an electron diffraction [13] study and was purified by repeated fractionation in a Vigreux column under reduced pressure. No impurity peaks were detected in a gas chromatographic analysis. Spectroscopic grade solvents (*Uvasole*) were used without further purification.

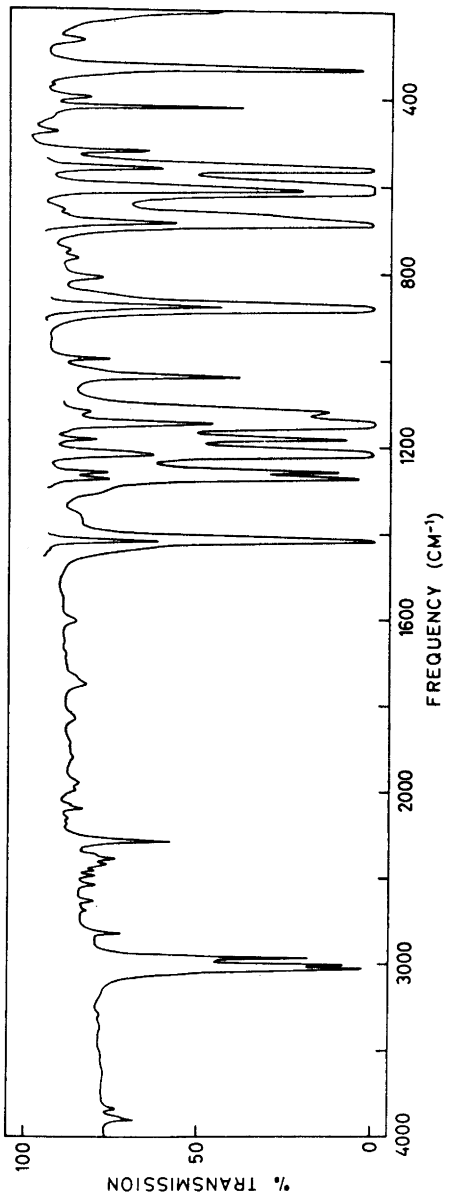

Fig. 1. The infrared spectrum of 1,1,2-tribromoethane in the liquid state.

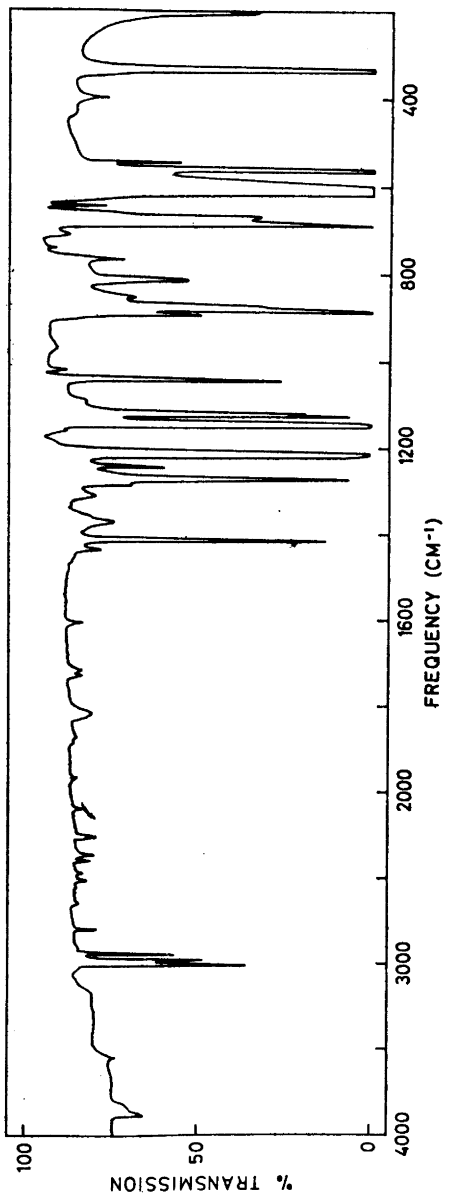

Fig. 2. The infrared spectrum of 1,1,2-tribromoethane in the crystalline state at −160°.

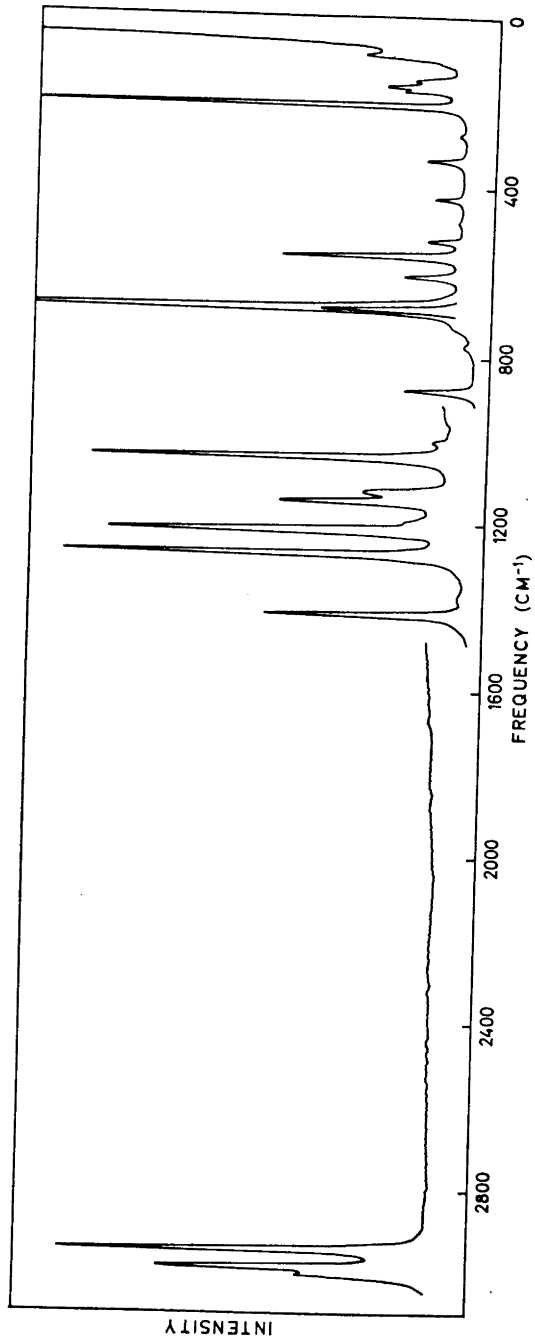

Fig. 3. The Raman spectrum of 1,1,2-tribromoethane in the liquid state.

The infrared spectra were recorded with a Perkin-Elmer model 225 spectrometer in the region 4000–200 cm^{-1}. Sealed cells of various thicknesses equipped with KBr, CsI, and polyethylene windows were used to record the spectra of the pure liquid and the solutions. A low temperature cell from RIIC equipped with CsI windows and cooled with liquid nitrogen was employed for the solid state spectra. Raman spectra were recorded with the aid of a Cary 81 spectrometer equipped with a Spectra Physics model 125 helium-neon laser. The pure liquid and the solutions were recorded using the silica capillaries in the axial illumination. Larger diameter tubes were used for the polarization measurements.

RESULTS AND DISCUSSION

The infrared spectra of the liquid and of the crystalline solid at $-160°$ in the region 4000–200 cm^{-1} are shown in Figs. 1 and 2, respectively. A plot of the Raman spectrum of the liquid is shown in Fig. 3. The observed frequencies of the band peaks (or shoulders) observed in the infrared and the Raman spectra are listed in Table 1. Our data agree well with the earlier infrared results,[5] but various shoulders and weaker bands not reported previously have been observed, and the frequency region extended with the modern grating spectrometer. Several new Raman bands were recorded and some uncertain bands reported previously[12] were not verified, and semiquantitative polarization measurements for the stronger bands were calculated. Since the present molecule has a quite low vapour pressure we did not make any serious attempt to record the vapour spectrum.

With 8 atoms the molecule should have 18 fundamental frequencies for each conformer. We have observed *ca.* 27 infrared and Raman bands of reasonable intensities which appear to be fundamentals. Thus, approximately half of the vibrational modes should be sufficiently separated for the two conformers to appear as distinct bands in the liquid spectra. For the remaining modes the close geometrical similarity between the conformers should result in coinciding (or overlapping) bands. This prediction is strongly supported by the number of liquid bands not present in the solid. Seven vanishing infrared bands have been observed (equipped with an asterisk in Table 1) above 250 cm^{-1} and are attributed to the conformer not present in the crystal.

One of the two staggered conformations of 1,1,2-tribromoethane should belong to point group C_s (pseudo *trans*). Two other spectroscopically identical forms should be present, having no symmetry element except identity (point-group C_1 or pseudo *gauche*) obtained by rotating one of the end groups an angle of 120° (or close to this value). The question remains, which of the two conformers are present in the crystal? Only the molecule with C_s symmetry should have any depolarized Raman bands, but this criterion is too uncertain to allow any definite conclusion. However, the two conformers will have widely different dipole moments, because of the high bond moment of the C–Br compared to C–H bonds. Therefore, the more polar form (C_s) should be stabilized relative to the less polar form (C_1) in solvents of high dielectric constants as expressed quantitatively by Onsager.[14] Approximately 20 % solutions were prepared of the ethane dissolved in the unpolar heptane and the highly polar acetonitrile. The infrared and the Raman spectra of 1,1,2-tribromoethane in these solvents were compared to the spectra recorded of

Table 1. Infrared and Raman spectral data for 1,1,2-tribromoethane.

Infrared Liquid	Infrared Solid	Raman Liquid	Conformer	Interpretation	
3895 w [a]	3891 } w 3870 }				
3020 s	3017 s	3024 m	I, II [b]	CH	stretch
3000 s	2997 s	3005 s P	I, II	CH	stretch
2959 s	2955 s	2962 s P	I, II	CH	stretch
2815 w					
	2804 w				
2680 w					
	2670 w				
2622 w					
2530 w	2528 w				
2480 w					
	2475 w				
2418 w					
	2410 w				
2382 w					
2287 m	2283 m				
2190 w					
1980 w					
1830 w					
1750 w	1748 w				
1733 vw	1733 w				
1440 sh	1438 w				
1418 s	1413 s	1421 m D	I, II	CH_2	scissor
1376 w	1372 w	1377 vw			
1312 sh	1315 w				
1286 m	1286 m				
1273 s	1271 s	1276 s P	II	CH	bend
1259 s	* [c]	1255 vw	I	CH	bend
1245 m	1245 m				
1217 s	1218 vs				
		1222 m P	II	CH_2	wag
1211 w	1209 vs				
1183 s	*	1195 vw	I	CH_2	wag
1165 vw					
1147 s	1146 vs	1150 w P	I, II	CH_2	twist
	1133 vw				
1121 m	1124 s	1130 w P	I, II	CH	bend
	1118 s				
	1095 vw				
1042 s	1042 s	1046 m P	II	CC	stretch
1025 vw	1025 vw				
1002 w	*	1007 w P	I	CC	stretch
	893 w				
885 vw					
879 s	882 vs	883 mP	I, II	CH_2	rock
	871 w				
856 sh	852 vw				
813 w	813 m				
769 w	767 w	770 vw			
750 vw	741 vw				
	708 w				

Table 1. Continued.

687 vs	683 vs	691 vs P	I, II	CBr	stretch
668 w	667 w				
610 vs	604 vs	613 s P	I, II	CBr	stretch
	590 w				
562 s	560 vs	566 vs P	II	CBr	stretch
	546 m				
524 m	*	529 s P	I	CBr	stretch
487 w	*	483 w P	I	273+208=481	
445 sh w					
424 m	*	428 m P	I	skel	deform
403 w	397 w	409 vvw	II	skel	deform
334 s	332 vs	338 s P	II	skel	deform
273 w	*	278 w D	I	skel	deform
208 m		208 vs P	I	skel	deform
		176 m P	II	skel	deform
		166 s D	II	skel	deform
		152 m D	I	skel	deform
		112 sh vw?			
		93 m D	I, II	CC	torsion

[a] The following abbreviations have been used. s, strong; m, medium; w, weak; v, very; sh, shoulder; P, polarized and D, depolarized.

[b] I denotes more polar conformer (C_s-symmetry) pseudo *trans*.
II denotes less polar conformer (C_1-symmetry) pseudo *gauche*.

[c] Bands disappearing in the crystal are marked with an asterisk.

the pure liquid. The ratios between the optical densities (Raman intensities) between various pairs of bands were calculated from the infrared (Raman) spectra and are listed in Table 2. It appears that the ratios diminish from heptane to acetonitrile while the pure liquid being moderately polar represents an intermediate value. The data reveal that the vibrational bands in the nominators should be attributed to the more polar conformer (C_s) and those in the denominator to the *less* polar form (C_1). Since the former class of bands disappear in the crystalline state (Table 1), the crystal therefore consists of molecules having C_1 symmetry. The same conclusion has previously been drawn [6] for the corresponding trichloroethane. All the earlier work on 1,1,2-tribromoethane indicated that the C_1-conformer was more stable than the C_s-conformer, amounting to 0.5 kcal/mole in the liquid state from infrared studies,[5] whereas dipole moment [8] and ultrasonic [10] data gave conflicting values. It is a well known fact the conformational energies in the ethanes are highly dependent on steric repulsion energies.[1-4] It is clear that steric repulsion from the three bulky bromine atoms in the C_s-conformer should greatly exceed that of the C_1-conformers in which the repulsion will be further diminished by a rotational angle larger than 120°. Because of the double weight of the C_1-conformer, a considerably higher concentration of this conformer should therefore persist in the liquid at room temperature, in agreement with the infrared and the Raman band intensities. Undoubtedly, the present molecule has a still higher enthalpy difference between the conformers in the vapour phase.

The vibrational spectra of this molecule were assigned on the basis of the bands vanishing in the crystal, the relative band intensities and the

Table 2. Intensity ratios for infrared and Raman band pairs of 1,1,2-tribromoethane dissolved in heptane and acetonitrile and in the pure liquid.

Ratio	Heptane	Liquid	Acetonitrile
E_{1273} [a]	3.8	1.8	0.7
E_{1259} / E_{1147} [a]	6.4	4.5	3.6
E_{1183} / E_{562} [a]	48.0	20.0	8.5
E_{524} / E_{334} [a]	5.0	1.8	1.5
E_{424} / I_{567} [b]	4.1	3.6	2.5
I_{529} / I_{338} [b]	5.0	3.2	1.5
I_{428}			

[a] Infrared bands, optical density.
[b] Raman bands, intensity.

variations with solvent polarity. Furthermore, our previous work on other halogenated ethanes containing bromine,[15,16] the frequencies reported for the corresponding trichloroethane [6] and the empirical group frequency correlations were of some help for the assignments.

The spectral interpretations are listed in Table 1 and for brevity, only certain important features will be discussed. Three strong infrared bands with Raman counterparts were observed in the liquid and in the crystal around 3000 cm^{-1} and they are the three CH stretching modes common for both the conformers. The infrared bands at 1418, 1147, 1121, and 879 cm^{-1} have corresponding Raman bands and persist in the crystal and are assigned to the various CH_2 scissoring, twisting, and rocking modes as well as the CH bending vibration coinciding for both the conformers. Band pairs at 1273 and 1259 cm^{-1}, at 1217 and 1183 cm^{-1}, and at 1042 and 1002 cm^{-1} are attributed to conformer II (C_1) and I (C_s), respectively. The latter pair are assigned to the C–C stretching mode.

Some very intense bands have been observed in the infrared as well as in the Raman spectra in the region 700–500 cm^{-1}. They are undoubtedly connected with the C–Br stretching vibrations, and we would expect them to be considerably influenced by the molecular geometry and therefore to appear as separate bands for each conformer. However, only one pair of bands at 562 and 524 cm^{-1} was detected, whereas the bands at 678 and 610 cm^{-1} must be common to both conformers. A puzzling problem is presented by the weak infrared band at 478 cm^{-1} vanishing in the solid, having a Raman counterpart at 483 cm^{-1} and thus belonging to conformer I. There is no other likely "mate" to this frequency for the conformer II, and it has therefore been assigned as a combination, $273+208=481$ cm^{-1}. The vibrational fundamentals below 450 cm^{-1} should involve various deformation vibrations between the bromine atoms and the carbon skeleton. The band pairs at 424 and 403

cm^{-1} and at 273 and 334 cm^{-1} have been verified from the crystalline spectra and the solvent studies. For the low frequency region the assignments are very uncertain since we did not have infrared data below 200 cm^{-1} and no Raman spectra of the solid. The interpretations listed in Table 1 seem reasonable and the sum and the product rules are fairly well satisfied. The 93 cm^{-1} Raman band was very distinct and agrees well with the torsional mode, whereas the 112 cm^{-1} shoulder was rather weak and doubtful.

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