

THE RAMAN SPECTRA OF 1, 1, 1- AND 1, 1, 2-
TRICHLOROETHANE IN THE SOLID STATE
AT -180°C^*

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Plate XIV

ABSTRACT. The Raman spectra of 1, 1, 1-trichloroethane and 1, 1, 2-trichloroethane in the solid state have been investigated and compared with those due to the two substances in the liquid state. It has been observed that in the case of 1, 1, 1-trichloroethane all the prominent Raman lines due to the liquid appear when the liquid is solidified, but in the case of the other molecule the two intense Raman lines 638 cm^{-1} and 786 cm^{-1} disappear with solidification of the liquid. A new Raman line 13 cm^{-1} appears with solidification of 1, 1, 1-trichloroethane and a similar new line 60 cm^{-1} has been also observed in the case of the other substance in the solid state. It has been also observed that some of the Raman lines due to the two liquids are totally depolarised. The significance of all these results has been discussed.

INTRODUCTION

The Raman spectra of many substituted ethanes have been investigated for different states of the substances and it has been observed that the number of Raman lines due to the solid state of these compounds is less than that of the lines due to the liquid state and such results have been interpreted by assuming that in the liquid state there are two forms of the molecules while in the solid state one of the two forms of the molecules disappears (Mizushima and Morino, 1938).

It has also been reported recently (Sheppard and Szasz, 1949) that even in the case of aliphatic hydrocarbons in the solid state, the number of Raman lines observed is much less than those observed in the case of the liquid, and such disappearance of some of the Raman lines on solidification

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has been interpreted on the assumption that in case of hydrocarbons also there are two forms of molecules in the liquid state and one of these two forms disappears with the solidification of the liquid.

The Raman spectra of 1, 1, 2-trichloroethane and 1, 1, 1-trichloroethane were not studied before in the solid state at low temperatures. The object of the present investigation is to find out whether the change in the relative positions of the chlorine atoms in the two molecules mentioned above influences the Raman spectra of these two substances in the solid state and also to find out whether any change in the structure of the molecules takes place with solidification at low temperatures. The polarisation of the Raman lines has also been studied in order to find out whether the molecules possess any symmetry.

EXPERIMENTAL

The liquids used were of C. P. quality and they were supplied by Eastman Kodak Co. They were repeatedly distilled in vacuum before exposure. A filter of 10% solution of NaNO_2 was used in the path of the incident light to cut off ultraviolet light, and this arrangement greatly reduced the intensity of fluorescence which was found to be produced by ultraviolet light.

In the case of 1, 1, 1-trichloroethane in the liquid state another filter of concentrated solution of NaNO_2 was used to reduce appreciably the intensity of the 4047 Å line, so that the assignment of the lines could be made correctly. The Raman spectra of the substances in the solid state were studied by solidifying the substances slowly in Pyrex containers which were gradually lowered in a transparent Dewar vessel containing liquid oxygen, and finally the lower portion of the container was completely immersed in liquid oxygen. A Fuess glass spectrograph was used to photograph the spectra and Ilford Zenith plates were used.

The polarisation of the Raman lines of the two liquids was studied in the usual manner by photographing the two components simultaneously with the help of a quartz double image prism. The polarisation of the Raman lines of carbon tetrachloride was also studied, using the same tube and the same arrangement, and from a comparison of these spectrograms the lines having degrees of polarisation of the order of 6/7 were found out.

RESULTS AND DISCUSSIONS

The spectrograms are reproduced in Plate XIV. The polarisation pictures are also reproduced to show that some of the lines are totally depolarised. The frequency shifts of the lines are given in Tables I and II.

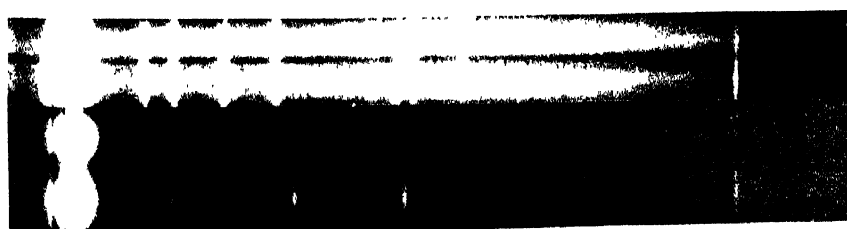
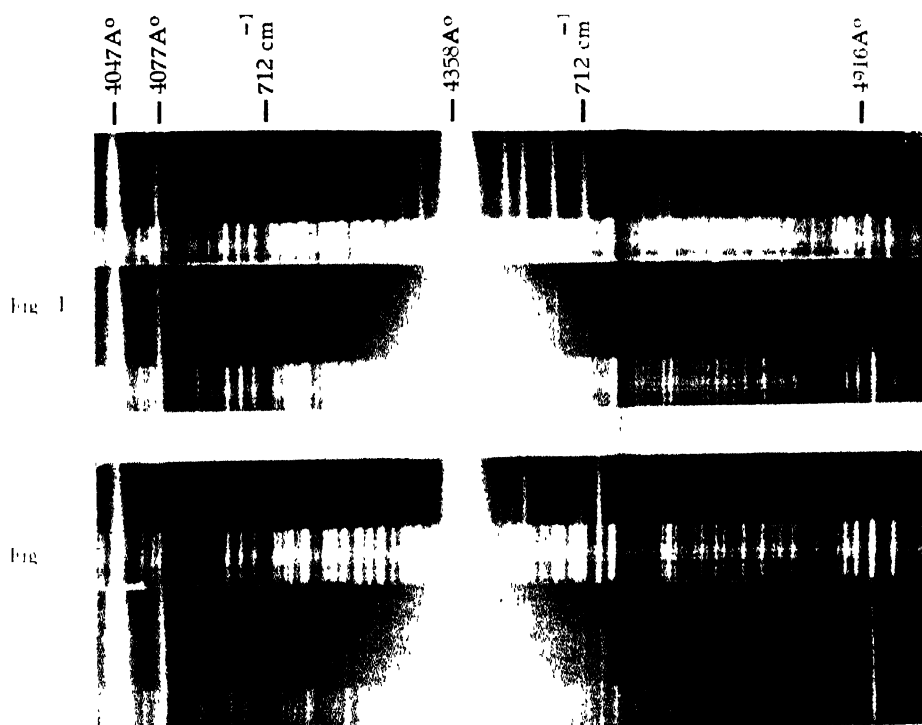


Fig. 3

Fig. 4

Raman Spectra

Fig. 1 (a). 1, 1, 1-Trichloroethane at 28° C
 .. (b) at -180° C

Fig. 2 (a) 1, 2-Trichloroethane at 28° C
 .. (b) at -180° C

Fig. 3 Polarisation of Raman lines
 (a) 1, 1, 1-Trichloroethane at 28° C.
 (b) 1, 1, 2 at 28° C

Fig. 4. Raman spectra (magnified) of 1, 1, 2-trichloroethane
 (a). at 28° C, (b). at -180° C.

TABLE I
1, 1, 1-Trichloroethane, $\Delta\nu$ in cm^{-1}

Liquid at 28°C		Solid at -180°C	
Hull (1934)	Present author	Present author	
* 241 (7)	241 (7), $\pm e, \pm k, i$; D	13 (2), k.	
* 345 (10)	345 (8), $\pm e, \pm k$; P	243 (2), e, k	
* 523 (9)	522 (10), $\pm e, \pm k$; P	347 (1), e, k	
712 (7b)	712 (5b), e, k; D	522 (4), e, k	
	973 (0), e; k; D	704 (2), e, k	
{ 1071 (2)	1067 (2), e, k; P		
1086	1082 (1), e, k; P	1072 (1b), e	
1175 (1)	1185 (0), k; ?		
1242 (1/2b)			
{ 1361 (1/2)			
1384			
{ 1424 (2)	1425 (2), e, k; D		
1451	1446 (2), e, k; D	1440 (0) ?	
1592 (1/2b)			
2743 (1/2b)			
2943 (7)	2939 (6), e, k, i; P	2937 (3), e, k	
3011 (6)	3007 (4), e, k; D	3007 (2), e, k	

Observed also as anti-stokes lines

TABLE II
1, 1, 2-Trichloroethane $\Delta\nu$ in cm^{-1} .

Liquid at 28°C		Solid at -180°C	
Hull (1935)	Present author	Present author	
	118 (2b) e, k; D	60 (2)	
	190 (1b) e, k; D	166 (1) e	
* 255 (4)	258 (4) $\pm e, k$; D	263 (1) e, k	
* 283 (2)	287 (2) $\pm e, k$; P		
* 332 (10)	333 (10) $\pm e, k$; P	338 (3) e, k	
* 395 (3)	391 (4) $\pm e, k$; P	385 (0) e	
* 441 (1/2)			
525 (1)	525 (2) $\pm e, k$; P	525 (0) e	
638 (3)	638 (4) $\pm e, k$; P	V	
664 (5b)	668 (6) $\pm e, k$; P	670 (3) e, k	
	697 (0) e, k; P		
	727 (0) e, k; P		
{ 772 (10)	775 (8) e, k; P	772 (6) e, k	
{ 781	786 (5) e, k; P	V	
931 (1)	934 (2) e, k; P	934 (0) e, ?	
1056 (1b)	1041 (1) e, k; P		
1207 (2)			
1260 (2)	1260 (2) e, k; D	1260 (0) e	
1304 (2)	1304 (3) e, k; P	1304 (0) e	
1428 (2)	1430 (3) e, D	1427 (1) e	
1475 (1/2b)			
2960 (8)	2961 (4) e, k, i; P	2961 (4) e, k	
2996 (7)	3001 (2) e, k; P	3005 (3) e, k	
3021 (5b)			

* Observed also as anti-stokes lines

It can be seen from Table I that in the case of 1, 1, 1-trichloroethane in the liquid state the lines 1232, 1361 and 1384 and 1592 cm^{-1} observed by Hull (1935) have not been observed in the present investigation. The spectrogram was a well exposed one, but no trace of these lines could be detected.

It is difficult to understand also how this molecule can yield a line 1592 cm^{-1} , because there is no C=C bond. In the spectrogram obtained by using a concentrated solution of sodium nitrite to absorb the 4047 Å line in the incident light, it was verified that the line 2743 cm^{-1} reported by Hull (1935) is actually a line 973 cm^{-1} excited by 4358 Å. The line 2743 cm^{-1} is not present in the spectrum. Similarly, the line supposed to be of frequency shift 1361 cm^{-1} excited by 4358 Å was found to be the line 2939 cm^{-1} excited by the line 4077 Å. Some of the lines due to the liquid are totally depolarised, and, therefore, the three-fold axis of rotation of the molecule is not disturbed in the liquid state.

In the solid state at -180°C this compound yields a new line at 13 cm^{-1} . This line is sharp but it is weak and cannot be due to the single molecule. It must be due to vibration of the whole molecule against other molecules in the lattice. Excepting the line 712 cm^{-1} the other lines do not shift with solidification of the liquid. This shows that in this particular case the intermolecular field in the solid state does not change the strengths of the bonds appreciably.

In the case of 1, 1, 2-trichloroethane in the liquid state the lines observed by Hull (1935) were observed in the present investigation except the lines 441, 1207 and 1575 cm^{-1} . This last line cannot be accounted for by assuming the known structure of the molecule. The lines 118 and 190 cm^{-1} were not observed by Hull (1915). These lines are fairly intense and they can be clearly seen in the spectrograms reproduced in the Plate XIV. They may be due to torsional and deformation oscillation respectively. The lines 697 and 727 cm^{-1} observed in the present investigation were not reported by Hull. The line 258 cm^{-1} probably due to deformation oscillation of the C-C group is totally depolarised. Hence the molecule has some elements of symmetry.

Since this line persists in the solid state also the molecule in the solid state has an element of symmetry and this element may be a plane of reflection. It is, however, surprising that the line 3001 cm^{-1} which might be due to antisymmetric C-H valence oscillation, is not totally depolarised, while the corresponding line due to 1, 1, 1-trichloroethane is totally depolarised. All the lines 638, 668, 697, 727, 775 and 786 cm^{-1} are found to be polarised. These lines are due to C-Cl oscillations. Of these six lines the two lines 668 and 697 cm^{-1} are extremely feeble. With the solidification of the liquid the lines 638 and 786 cm^{-1} disappear and owing to the feebleness of the lines 668 and 697 cm^{-1} it could not be ascertained whether they

also disappear with solidification. The line 287 cm^{-1} also is seen to disappear with solidification. Such a disappearance of some of the lines was interpreted by previous workers in the case of disubstituted ethanes on the assumption that two types of molecules are present in the liquid and one of the two types transforms itself into the other type with solidification. In the case of ethylene dibromide, for instance, (Mizushima and Morino, 1938) some of the lines due to C-H valence and deformation oscillation also disappear with solidification along with a few lines due to C-Br oscillation. In the case of 1, 1, 2-trichloroethane, on the other hand, all the lines due to C-H valence and deformation oscillation persist when the liquid is solidified. This can happen only when the two types of molecules have the same frequencies for C-H oscillations, but in that case the frequencies of C-Cl vibration in the two types would not be so different from each other.

The appearance of the feeble line 60 cm^{-1} in the case of the solid state may indicate formation of a dimer. It is significant that the line 190 cm^{-1} probably, due to C-Cl deformation oscillation shifts to 166 cm^{-1} with solidification of the liquid. However, the influence of intermolecular field in the liquid on the strength of the bonds can be determined only by studying the Raman spectrum of the substance in the vapour state. It has been observed by Mizushima, Morino, Watanabe, Simanouti and Yamaguchi (1949) that the intensity of those Raman lines of ethylene dichloride which disappear with solidification of the substance also diminishes when the substance is converted to vapour. This fact indicates a complicated influence of intermolecular field on the strength of the C-Cl bonds and the study of several such substances in the vapour state is necessary before definite conclusion can be drawn.

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