

POLARISATION OF RAMAN LINES OF ETHYLENE DIBROMIDE IN SOLUTION AND INTENSITIES AT DIFFERENT TEMPERATURES \*

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Plates VIII A and VIII B

**ABSTRACT.** The polarisation of the Raman lines of solutions of ethylene dibromide in methyl alcohol, benzene, toluene, carbon tetra-chloride and hexane has been studied. It is observed that the line  $1056\text{ cm}^{-1}$  is totally depolarised in the case of the solutions in all the solvents except in hexane. In the latter case the line  $1056\text{ cm}^{-1}$  is observed to be only partially polarised. The ratio of the intensities of the lines  $551\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  of ethylene dibromide in the liquid state at about  $12^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$  and  $95^{\circ}\text{C}$  has also been determined experimentally. It is observed that this ratio remains almost the same as the liquid is cooled down from the room temperature up to  $12^{\circ}\text{C}$  and it diminishes slightly when the temperature is raised to  $95^{\circ}\text{C}$ . It is pointed out that these facts are contradictory to the hypothesis put forward by Mizushima and co-workers regarding the origin of the line  $551\text{ cm}^{-1}$  and can be explained by assuming the existence of strongly associated molecules in the liquid.

INTRODUCTION

The Raman spectra of pure ethylene dichloride and dibromide in the liquid state at room temperature and in the solid state at low temperatures were studied previously by Mizushima *et al* (1934, 1936) and the results were explained on the hypothesis that in the solid state all the molecules are in the trans configuration and in the liquid state there are two forms—one trans and other as having no centre of symmetry. The lines  $1056\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$  were expected to be polarised according to their hypothesis. Sirkar and Bishui (1945) repeated the investigations and on studying the polarisation of the Raman lines pointed out that the two lines mentioned above are actually totally depolarised and therefore the explanation offered by Mizushima and Morino (1938) was not satisfactory. They further suggested that in the liquid state some of the ethylene dibromide molecules might be in an associated state forming thereby groups having the symmetry  $C_{2v}$  and in the solid state the group might change to one having a symmetry  $D_{2h}$ .

Later Bishui and Sanyal (1947) studied the relative intensities of the lines  $660\text{ cm}^{-1}$  and  $551\text{ cm}^{-1}$  of the ethylene dibromide dissolved in different solvents. On comparing the results with those published earlier by Mizu-

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shima, Morino and Higasi (1934) regarding this intensity ratio and the permanent electric moment of the molecule it was concluded by them that the results could not be explained by assuming the presence of two types of single molecules of ethylene dibromide having different symmetry elements in the solutions. They tried to explain the results by assuming the presence of associated molecules having only a plane of symmetry in the pure liquid. If the associated molecules break up into single molecules when ethylene dibromide is dissolved in any solvent, it is expected according to the hypothesis put forward by Sirkar and Bishui (1945) that the line  $1056\text{ cm}^{-1}$  due to C-C valence oscillation should not be totally depolarised in the case of such a solution. In order to investigate this question the polarisation of the Raman lines of ethylene dibromide dissolved in benzene, toluene, carbon-tetrachloride, hexane and methyl alcohol has been studied in the present investigation. Since some of the prominent lines due to carbon-tetrachloride, benzene and toluene are totally depolarised, by comparing the depolarisation of these lines with that of the line  $1056\text{ cm}^{-1}$  it is also possible to ascertain easily whether the line  $1056\text{ cm}^{-1}$  of ethylene dibromide dissolved in these solvents is actually totally depolarised or not. Hexane has been chosen as one of the solvents because Mizushima *et al* (1934) and later Bishui and Sanyal (1947) observed that the line  $551\text{ cm}^{-1}$  of ethylene dibromide diminishes in intensity when the liquid is dissolved in hexane.

If the hypothesis put forward by Mizushima *et al* that the relative proportion of molecules of trans and other configuration present in the liquid is dependent upon temperature be true it is expected that the ratio of the intensities of the lines  $551\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  will increase at high temperature. In order to test the hypothesis, the Raman spectra of ethylene dibromide in the liquid state have been studied at three different temperatures, *e.g.*, at  $12^\circ\text{C}$ , *i.e.*, two degrees above melting point, at the room temperature and at about  $95^\circ\text{C}$ . These results also have been discussed in the light of the hypothesis put forward by previous workers.

#### EXPERIMENTAL

Kahlbaum's pure ethylene bromide was available from old stock in the laboratory for the present investigation. The solvents also were taken from Kahlbaum's or Merck's original packings. All the liquids had to be redistilled in vacuum in order to get rid of fluorescence. The molecular concentrations of ethylene dibromide in the solutions used were as follows: in methyl alcohol 0.19, in carbon tetrachloride 0.35, in benzene 0.35, in toluene 0.55 and in hexane 0.43 and 0.37. The purity of the solvents was tested by photographing their Raman spectra. The Fuess Spectrograph used in the previous investigations was employed in the present investigations also.

In order to study the polarisation of the Raman lines the light from a mercury arc was focussed on the Wood's tube containing the solution and the vertical and horizontal components of the scattered light were photo-

graphed simultaneously. It was easy in the case of solutions to find out whether a particular line was totally depolarised or not by comparing the relative intensities of its horizontal and vertical components with those of a known totally depolarised Raman line of the solvent. The convergence of the incident light and the weakening of the vertical component during passage through the spectrograph only made the horizontal component stronger, but the comparison mentioned above was not rendered difficult by such an increase in the intensity of the horizontal component. The comparison was made by taking microphotometric records of the horizontal and vertical components of the Raman lines with the help of a Moll's self recording microphotometer.

In order to study the relative intensities of the lines  $551\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  at different temperatures, a Wood's tube of Pyrex glass provided with a flat thin window was surrounded by a jacket of Pyrex glass. Water cooled in a reservoir by melting ice up to about  $12^{\circ}\text{C}$  was circulated with the help of a pump through the jacket throughout the exposure and the Raman spectrum of pure ethylene dibromide, sealed inside the Wood's tube and maintained at a temperature of  $12^{\circ}\text{C}$ , was photographed using the spectrograph mentioned above. Next the Raman spectrum of the liquid at the room temperature (about  $30^{\circ}\text{C}$ ) was photographed on a plate taken from the same packet. Finally steam was passed continuously through the jacket and the Raman spectrum of the liquid thus kept at a temperature of about  $95^{\circ}\text{C}$  was photographed on another plate taken from the same packet. The microphotometric records of the lines  $551\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  were taken in all the three cases. Ilford 'Selochrome' plates were used in the present investigation. The relative intensities of the lines  $551\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  were determined with the help of a blackening log-intensity curve drawn by taking intensity marks using a tungsten filament lamp and different widths of the slit of the spectrograph.

#### RESULTS AND DISCUSSION

The microphotometric records of the horizontal and vertical components of the Raman spectra of solution of ethylene dibromide in carbon tetrachloride and hexane are reproduced in figures 1 and 2, Plate VIIIA and the spectrograms for all the solutions are reproduced in Plate VIIIB. It will be observed from Fig. 1 that the line  $314\text{ cm}^{-1}$  of carbon tetrachloride, which is totally depolarised, has got both the horizontal and vertical components almost equally intense in the arrangement used for photographing them. In fact the horizontal component is slightly weaker than the vertical component. At the same time the horizontal and vertical components of the line  $1056\text{ cm}^{-1}$  of ethylene dibromide in the solution are of the same intensity. This definitely proves that this line of ethylene dibromide is totally depolarised because the factor of depolarisation of the line  $314\text{ cm}^{-1}$  of carbon tetra-

chloride is about 0.8. The spectrograms reproduced in the Plate VIII B also show that this line is totally depolarised in solutions in benzene, methyl alcohol, and toluene. On the other hand from Figure 2, Plate VIII A, it appears that the horizontal component of the line  $1460\text{ cm}^{-1}$  is about twice as intense as the vertical component while the horizontal component of the  $1056\text{ cm}^{-1}$  line is only slightly more intense than the vertical component in the arrangement used to photograph this Raman spectrum. Hence if the line  $1460\text{ cm}^{-1}$  be totally depolarised the line  $1056\text{ cm}^{-1}$  is only partially depolarised.

Hence as the molecules of ethylene dibromide are dissolved in hexane not only the intensity of the line  $551\text{ cm}^{-1}$  but also the factor of depolarisation of the line  $1056\text{ cm}^{-1}$  diminishes appreciably. If the line  $551\text{ cm}^{-1}$  were due to the vibration of a molecule of the *gauche* configuration, as suggested by Mizushima *et al* (1942), the diminution of intensity of this line in the solution would indicate an increase in the number of molecules in the trans configuration in the solution, but the line  $1056\text{ cm}^{-1}$  due to the C-C valence oscillation of the single molecule, either of the trans configuration or of any other rotational isomer, could never be totally depolarised. Hence the results cannot be explained on the hypothesis put forward by Mizushima *et al*. On the other hand if it is assumed that in the pure liquid the molecules are mostly associated and the group formed in this way has a plane of symmetry, as suggested by Sirkar and Bishui (1945), the line  $1056\text{ cm}^{-1}$  is expected to be almost totally depolarised in the pure liquid. In the solution in hexane some of the associated groups probably break up into single molecules as indicated by the diminution of the intensity of the line  $551\text{ cm}^{-1}$  and the number of single molecules thereby increases. Since the line  $1056\text{ cm}^{-1}$  due to the C-C oscillation of a single molecule cannot be totally depolarised the value of factor of depolarisation of this line in solution is expected to be less than 6/7. Thus all these observed facts can be explained on the hypothesis put forward by Sirkar and Bishui and it is difficult to explain them on the hypothesis put forward by Mizushima *et al* (1934).

TABLE I

Temperature	$I_{660} : I_{551}$
$12^{\circ}\text{C}$	100 : 17
$30^{\circ}\text{C}$	100 : 18
$95^{\circ}\text{C}$	100 : 15

The microphotometric records of the Raman spectra of ethylene dibromide at  $12^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$  and  $95^{\circ}\text{C}$  are reproduced in Fig. 8. As regards the relative intensities of the lines  $551\text{ cm}^{-1}$  and  $660\text{ cm}^{-1}$  at different temperatures the values estimated are given in Table I. The value for  $12^{\circ}\text{C}$  is only approximate because due to opalescence of the liquid at a temperature just above

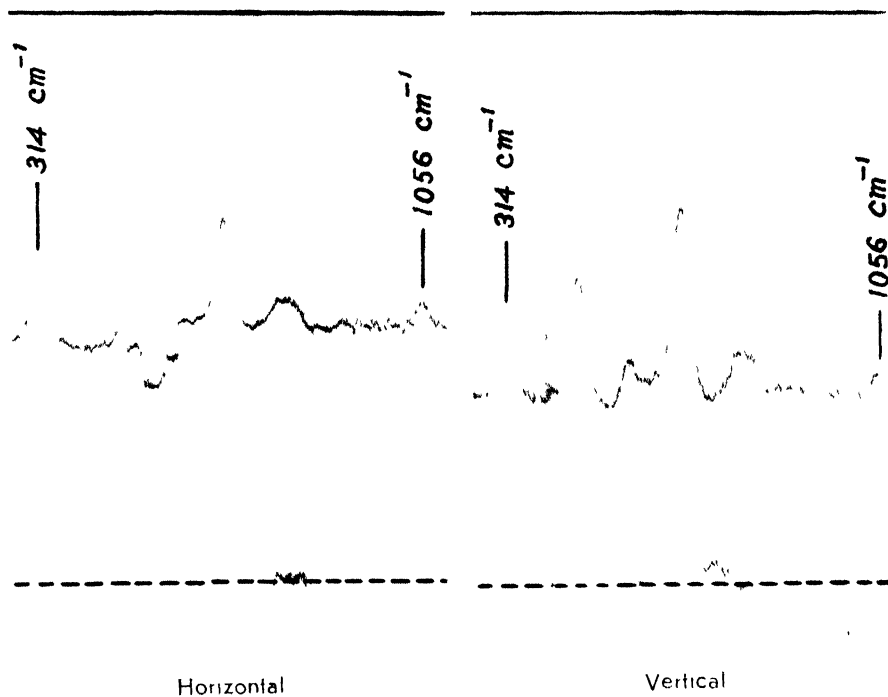


Fig. 1

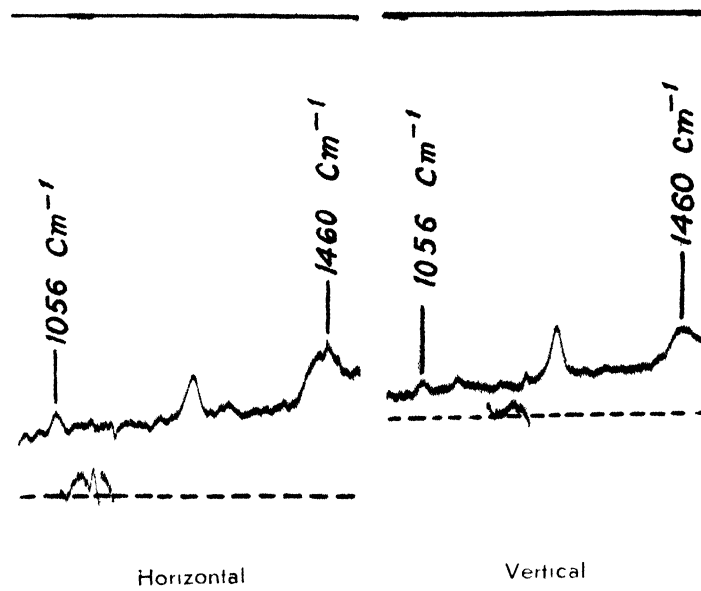
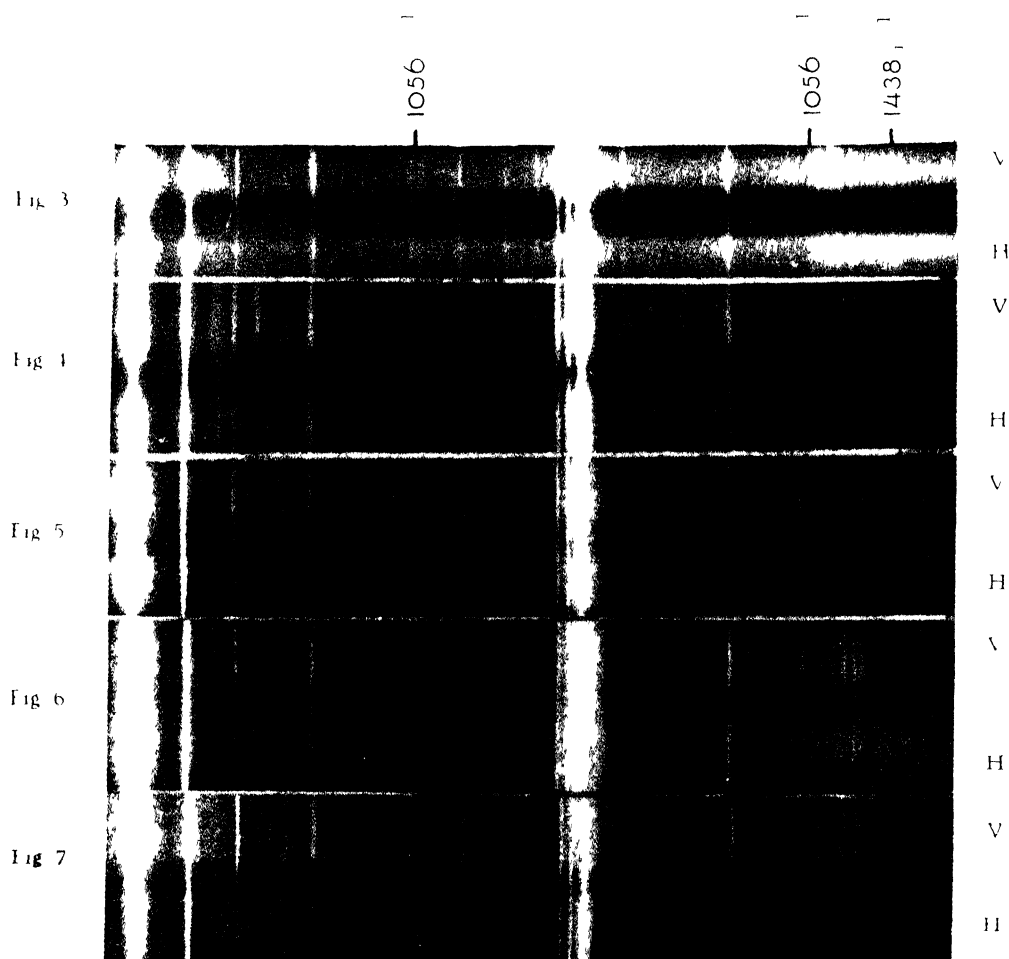


Fig. 2

Polarisation of Raman lines of ethylene dibromide in solution.



Polatisation of the Raman lines

Fig 3	$C_2H_4Br_2$	$C_2H_4$	M lar Con	= 0.13
Fig 4		$CCl_4$	-	0.34
Fig 5		$C_6H_6$	-	0.35
Fig 6		$CH_2$	=	0.55
Fig 7		$CH_2OH$		0.19

the melting point there was continuous background in the spectrum of the scattered light.

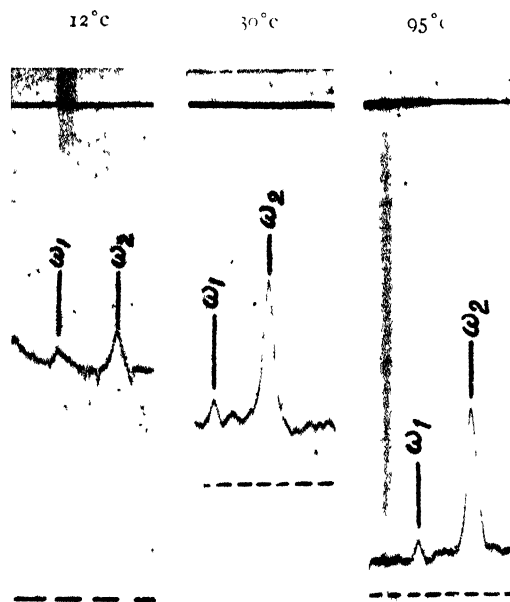


FIG. 8

Microphotometric records of Raman spectra of  
ethylene dibromide

$$\omega_1 = 551 \text{ cm}^{-1}$$

$$\omega_2 = 660 \text{ cm}^{-1}$$

It can, however, be seen from Table I that the relative intensity of the line  $551 \text{ cm}^{-1}$  does not diminish remarkably at  $12^\circ\text{C}$  and also it does not increase at  $95^\circ\text{C}$ . This fact is contradictory to the hypothesis put forward by Mizushima *et al* (1934, 1942) that this line is due to a configuration of the molecule other than trans and that the number of such molecules increases with increase of temperature of the liquid. The observed facts, can on the other hand be explained by assuming that the line  $551 \text{ cm}^{-1}$  is due to a vibration in the strongly associated molecule and that the number of such molecules diminishes with increase of temperature. In the case of vapour the number of such associated molecules is expected to diminish still further and thus the line  $551 \text{ cm}^{-1}$  is expected to diminish in intensity still further. It has actually been observed by Morino, Watanabe and Mizushima (1942) that the line  $551 \text{ cm}^{-1}$  is almost absent in gaseous ethylene dibromide. The results obtained by them in the case of the vapour therefore support the hypothesis put forward by Sirkar and Bishui that the line is due to the vibration of an associated molecule and are contradictory to the hypothesis put forward by Mizushima *et al* (1934) that it is due to a form of the molecule other than the trans configuration.

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