ON THE RAMAN SPECTRA OF SOLUTIONS OF ETHYLENE DIBROMIDE IN DIFFERENT SOLVENTS *

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(Plate VI)

ABSTRACT, The Raman spectra of moderately dilute solutions of ethylene dibromide in different solvents, e g., methyl alcohol, carbon tetrachloride, benzene, toluene and hexane have been studied and the relative intensities of the Raman lines 551 cm⁻¹ and 660 cm⁻¹ have been determined with help of blackening-log-intensity curves in each case as well as in the case of the pure liquid. The values of the ratio I₆₆₀·I₅₅₀ observed in the different cases are as follows. For pure liquid it is 100·17.4, for solution in methyl alcohol 100·24, in carbon tetrachloride, 100:17, in benzene, 100·23, in toluene 100:22 and in hexane it is 100:10. These results have been discussed in the light of the hypotheses put forward by Mizushima etal (1934) and by Sirkar and Bishui (1945). It is pointed out that it is difficult to explain all the observed facts with the help of the former hypothesis.

INTRODUCTION

The permanent electric moment (m) of ethylene dichloride and ethylene dibromide dissolved in different solvents was measured by Mizushima, Morino and Higasi (1934), the solvents used for the purpose being hexane, heptane, ether, benzene, toluene and amylene in the former case and hexane, benzene, carbon disulphide and carbon tetrachloride in the latter case. It was observed by them that the value of m for $C_2H_4Cl_2$ increases from the value 1.14×10^{-18} at $-70°C$ to about 1.38×10^{-18} at about $30°C$ in the case of solutions in hexane, heptane and amylene, while it remains almost constant at different temperatures in the solutions in benzene and toluene, the values in these two cases being 1.75×10^{-18} and 1.7×10^{-18} respectively. In order to explain this dependence of m on temperature they have assumed that the CH_2Cl group in the $C_2H_4Cl_2$ molecule is always executing rotatory oscillations about the trans configuration, the angular amplitude ϕ of this oscillation being determined by the Maxwell Boltzmann distribution law. The potential energy U has been assumed to be equal to $\beta (1 - \cos \phi)$ and different values have been given to β in the case of different solvents in order to explain the observed variation of m with temperature. The higher value of m observed in the case of benzene is explained on the assumption that benzene acts as a polar solvent and the value of ϕ is very large for the majority of the molecules

in solution in benzene as in the solutions in methyl alcohol or ether. They could not, however, explain satisfactorily why the value of m of the $C_2H_4Cl_2$ molecule dissolved in benzene is independent of temperature and is only slightly larger than that observed in the case of solution in hexane, although the value of the ratio $I_{653} : I_{759}$ in the latter case is only one third that in the former case. It was, therefore, thought worth while to determine the relative intensities of the corresponding Raman lines of $C_2H_4Br_2$ dissolved in different solvents, employing the more accurate method of photographic photometry in order to understand the significance of the changes obseived with the change in the solvent.

<div align="center">E X P E R I M E N T A L</div>

Kahlbaum's pure ethylene dibromide was used in the present investigation. It was distilled in vacuum before it was used for making the solutions. The solvents were also obtained either from Merck's or from Kahlbaum's original packing and each of them had to be distilled repeatedly in vacuum in order to get rid of continuous background in the Raman spectra. The molecular concentrations of $C_2H_4Br_2$ in the solutions in different solvents are: in benzene 0.35, in toluene 0.55, in hexane 0.43, in methyl alcohol 0.19 and in carbon tetrachloride 0.35. The Raman spectra of the pure liquid and of the solutions were photographed on Ilford Selochrome plates taken from the same packet and the plates were developed under identical conditions. A Fuess spectrograph with optical parts of glass was used. The intensity marks were taken on some of the plates, using different known slit-widths and a strip of white card board illuminated by light from a tungsten filament lamp as source of light. The purity of the solvents was tested by photographing their Raman spectra. Microphotometric records were then obtained for the lines 551 cm^{-1} and 660 cm^{-1} in all the spectrograms and also for the intensity marks, using a Moll's self-registering microphotometer. For the pure liquid spectrograms with different times of exposure were obtained in order that the density of the line 660 cm^{-1} in the spectrograms due to the mixtures might be almost the same as that in one of these different spectrograms for the pure liquid.

Blackening-log-intensity curves were then drawn-for the wavelengths corresponding to the lines 551 cm^{-1} and 660 cm^{-1} excited by the Hg line 4358 A. U. and with the help of the blackening-log-intensity curves the relative intensities of these two lines were determined in each case. If I_1 and I'_1 be the intensities of the line 551 cm^{-1} in the spectrograms due to the pure liquid and one of the solutions respectively, and I_2 and I'_2 those for the line 660 cm^{-1}, we have

$$I_1/I'_1 = c_1, \quad I_2/I'_2 = c_2$$

$$\therefore \quad \frac{I_1}{I_2} = \frac{c_1}{c_2} \cdot \frac{I'_1}{I'_2}.$$

Thus it is easy to find out whether the ratio $\frac{I_1}{I_2}$ undergoes any change on dissolving the liquid in any solvent.

In determining the intensities of the lines, the total intensity at the peak of the line and that of the background were found out. On subtracting the latter from the former, the true intensity of the line was obtained. While obtaining the microphotometric records, the deflection due to the unexposed part of the plate was recorded, so that the intensity of the background referred to this unexposed part could be determined. The line of infinite density was also recorded on all the records. Some of these microphotometric records are reproduced in Plate VI. It can be seen from Figs. 1 and 2 that the ratio $I_{551}:I_{660}$ is less in the case of hexane than in the pure liquid. The actual values observed in the different cases are given in Table I.

TABLE I
Ethylene dibromide

State	$I_{660}:I_{551}$	$m \times 10^{-18}$
Pure liquid	100 : 17.5	......
Solution in CCl_4	100 : 17	0.86 (20°C)
Solution in CH_3OH	100 : 24	......
Solution in benzene	100 : 23	1.18 (20°C) 1.20 (50°C)
Solution in toluene	100 : 22	......
Solution in hexane	100 : 10	0.91 (25°C) 0.79 (0°C)

The values of permanent electric moment m observed in the different cases by Mizushima *et al* (1934) are given in the last column of Table I. The corresponding results obtained in the case of ethylene dichloride by those authors are given in Table II for comparison.

TABLE II
Ethylene dichloride

State	$I_{652}:I_{653}$	$m \times 10^{-18}$
Pure liquid	100 : 71	1.12 × (gas at 30°C)
Solution in CH_3OH	100 : 83	......
Solution in ethyl alcohol	100 : 75	......
Solution in ether	100 : 50	1.49 (20°C)
Solution in hexane	100 : 20	1.36 (25°C)
Solution in benzene	100 : 67	1.75 (30° − 50°C)

It can be seen from Table I that the ratio $I_{551}:I_{660}$ increases considerably when ethylene dibromide is dissolved in methyl alcohol, benzene or toluene, but it remains unchanged when carbon tetrachloride is used as the solvent. Again in solution in hexane the value of the intensity ratio diminishes to about half the original value. The values of m given in the last column can not be reconciled with those of this intensity ratio on the hypothesis put forward by Mizushima *et al* (1934) that the number of molecules in the trans configuration diminishes when the liquid is dissolved in solvents of high dielectric constant and the lines 660 cm^{-1} and 551 cm^{-1} are the corresponding lines due to the trans and oscillating configurations of the molecule respectively. The trans configuration has no permanent electric moment and the value of m in the case of solution in hexane is slightly higher than that for solution in carbon tetrachloride. Hence according to the hypothesis put forward by Mizushima *et al* (1934) the ratio $I_{551}:I_{660}$ ought to have been slightly higher in the case of solution in hexane than in the solution in carbon tetrachloride. On the contrary the ratio is observed to be 1:10 in the former case which is less than 1.7:10 observed in the latter case. Such a discrepancy also occurs in the case of ethylene dichloride as can be seen from results reported by Mizushima *et al* (1934) and quoted in Table II. In the case of solution in benzene the corresponding ratio $I_{653}:I_{752}$ is 1:1.5 and the value of m is 1.75×10^{-18}, but in the case of solution in hexane the ratio is 1:5 while the value of m is 1.36×10^{-18}. Since the permanent moment is wholly due to the molecules in the configuration other than the trans configuration the value of m in solution in hexane ought to have been much less than 1.36×10^{-18}. It has been pointed out by them that this anomaly is not due to the presence of associated molecules of $C_2H_4Cl_2$ in the solution in benzene, because according to the cryoscopic measurements carried by Harada* the molecule has normal molecular weight in dilute solution in benzene. They have not, however, given any satisfactory explanation of this anomaly.

The hypothesis put forward by Mizushima *et al* (1934) mentioned above cannot explain also some changes in the Raman spectra which are observed when these two liquids are solidified at low temperatures. If the Raman lines which disappear with the solidification of the liquids would be due to the non-planar configurations of the molecule and those which persist in the solid state be due to the trans configuration, we would expect the lines which disappear to be polarised because the non-planar configurations, have no symmetry element and they do not postulate the existence of large number of molecules of this type in the liquid state. Actually, however, some of the lines which disappear in the solid state are totally depolarised in the liquid state. Again the line 3012 cm^{-1} which is totally depolarised in the liquid state is evidently due to some antisymmetric valence

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oscillation of the C-H groups. This line persists in the solid state, but such an oscillation is totally forbidden in the Raman effect in the case of the trans configuration. Hence this line cannot be due to any antisymmetric oscillation of the single $C_2H_4Cl_2$ molecule in the trans configuration. We have, therefore, to assume the existence of some other configuration of the molecule in the liquid and solid states to explain these observed facts.

It has already been pointed out by Sirkar and Bidari (1945) that the presence of associated molecules may be responsible for the changes in the Raman spectra which occur with the change of state of these substances. As regards the change in the relative intensities of the lines 551 cm^{-1} and 651 cm^{-1} of ethylene dibromide observed in the present investigation it can be seen that if the line 651 cm^{-1} is due to the associated molecules, the number of such molecules increases when the liquid is dissolved in benzene, toluene and methyl alcohol and it diminishes when hexane is used as the solvent. The permanent electric moment, however, remains almost unchanged when the liquid is dissolved in hexane
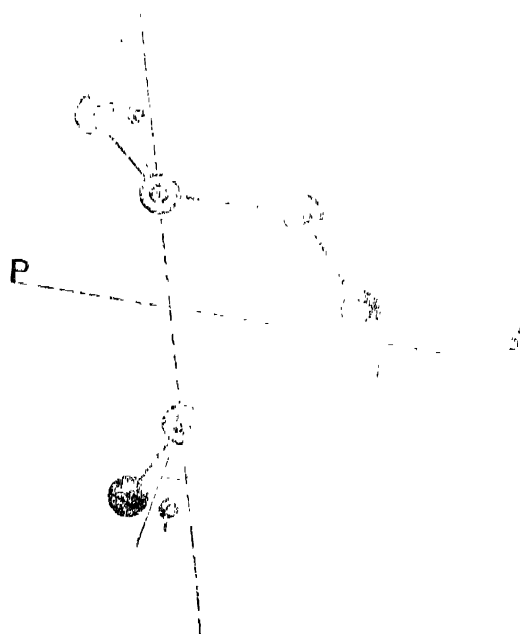
Fig. 8

and it increases in solutions in benzene, toluene and methyl alcohol. We have, therefore, to assume the shape of the associated molecule in solution in benzene to be non-planar as shown in Fig. 8 so that the value of m for the single molecule is much less than that for the cis configuration but the value of m for the associated molecule being the resultant of two such moments inclined at an angle slightly less than 90°, is greater than that for the single molecule. The increase in the value of m with temperature may be due to the increase in the angle ϕ made by the C-CH$_2$Cl plane with the plane of trans configuration. In the case of solution in cyclohexane the angle of inclination of the permanent moments of the two constituent $C_2H_4Cl_2$ molecules with each other at about 20°C is such that the value of the resultant moment is almost the same as that for the single molecule. Hence the value of m does not change appreciably even when the number of associated molecules diminishes. With the rise of temperature the angle diminishes slightly so that the value of the resultant increases a little. It may also so happen that the value of ϕ is larger in the solution in hexane than in the pure liquid.

Thus the observed facts can be explained by assuming the existence of associated molecules of static model postulated by Sirkar and Bishui (1945). In the solid state probably the structure of the molecule changes to a centro-symmetrical one as pointed out by them. On the other hand the structure postulated by Mizushima et al is of dynamic type oscillating about the trans configuration. There is other difficulties besides those mentioned above in postulating the existence of molecules of such a dynamic structure. The frequencies of such rotatory oscillations of the molecules about the trans configuration are expected to be much higher than that of the applied electric field used in the measurement of dielectric constant, as can be seen from the values of β given by Mizushima et al (1934). Hence only the mean square value of m is expected to be observed from the polarisation measured experimentally. They have assumed that the value of m is given by

$$m^2 = 4\mu^2\sin^2\theta \cdots \frac{\displaystyle\int_{-\pi}^{+\pi} e^{-U/kT}\sin^2\frac{\phi}{2}\,d\phi}{\displaystyle\int_{-\pi}^{+\pi} e^{-U/kT}\,d\phi} \qquad \cdots \text{(1)}$$

where θ is the angle between the C-C line and the dipole moment of CH_2Cl or CH_2Br group, μ is the moment of the group and $U = \beta\,(1-\cos\phi)$. It is evident that equation (1) gives the value of m^2 only when the static model is assumed and the value of ϕ is governed by the Maxwell-Boltzmann distribution law. The value of m^2 for the dynamic model oscillating with frequency higher than that of the applied field is not given by (1). Hence the values of m calculated by them with the help of (1) cannot be those for the dynamic model.

The relative intensities of the Raman lines $653\ cm^{-1}$ and $752\ cm^{-1}$ of ethylene dichloride dissolved in various solvents are being measured with the help of blackening log intensity curves and the discussion of the results obtained for that substance by Mizushima et al is reserved for a future communication.

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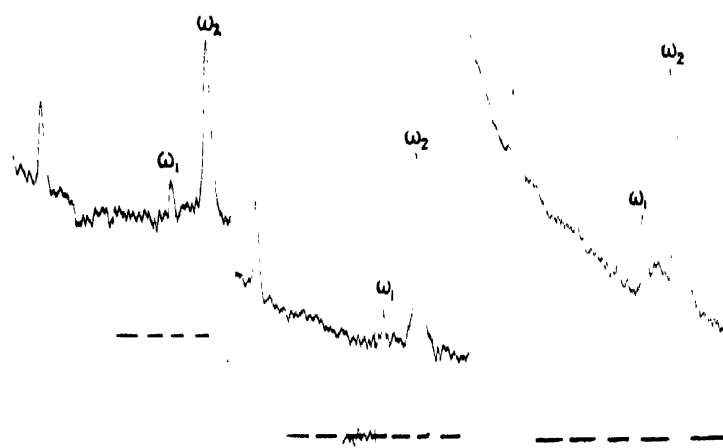Sirkar, S. C. and Bishui, B. M. (1945), *Ind. J. Phys.*, **19**, 24.
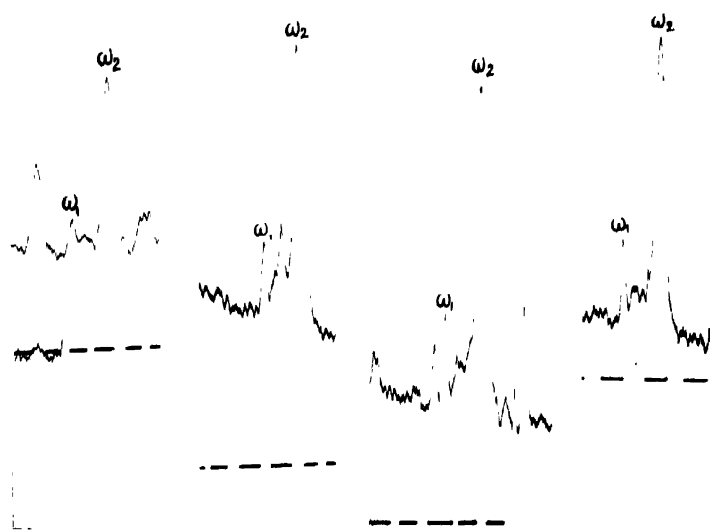
Fig. 1   Fig. 2   Fig. 3

Fig. 4   Fig. 5   Fig. 6   Fig. 7

MICROPHOTOMETRIC RECORDS OF RAMAN SPECTRA.

Fig. 1   Pure $C_2H_1Br_3$ Fig. 5   Solution in C_6H_6

Fig. 2   Solution in hexane   Fig. 6   ,,   ,, toluene

Fig. 3   ,,   ,, CH_3OH Fig. 7   Pure $C_2H_1Br_3$

Fig. 4   ,,   ,, CCl_4 $\omega_1 = 551 cm^{-1}$, $\omega_2 = 660 cm^{-1}$

PLATE VI

Fig. 1 Fig. 2 Fig. 3

Fig. 4 Fig. 5 Fig. 6 Fig. 7

MICROPHOTOMETRIC RECORDS OF RAMAN SPECTRA.

Fig. 1 Pure C_2H_5Br.
Fig. 2 Solution in hexane
Fig. 3   "   " CH_3OH
Fig. 4   "   " CCl_4

Fig. 5   Solution in C_6H_6
Fig. 6   "   " toluene
Fig. 7   Pure C_2H_5Br.

$\omega_1 = 551 cm^{-1}$, $\omega_2 = 660 cm^{-1}$