

ON THE RAMAN SPECTRA OF ETHYLENE DIBROMIDE AND DICHLOROETHYLENE IN THE SOLID STATE

BY S. C. SIRKAR* AND B. M. BISHUI

(Plate III)

ABSTRACT. The Raman spectra of ethylene dibromide and mixture of *cis* and *trans* dichlorethylene in the solid state at -170°C have been studied and these Raman spectra have been compared with those for the liquid state. The polarisation of the Raman lines of ethylene dibromide in the liquid state has also been studied. It is pointed out that two of the intense Raman lines of liquid ethylene dibromide which ought to have been polarised according to the hypothesis put forward by Mizushima and Morino (1938a) are actually depolarised. A new explanation that the liquid state of ethylene dibromide consists of pairs of *cis* molecules forming a configuration having a symmetry C_{2v} is offered and its advantages over the former one are discussed. It is assumed that in the solid state the configuration changes to have the symmetry of the point group D_{2h} and the observed variation of the permanent electric moment with change of state is also explained on this hypothesis.

INTRODUCTION

It was first observed by Mizushima, Morino and Noziri (1936) that some of the Raman lines of ethylene dichloride and ethylene dibromide observed in the liquid state disappear when the liquids are solidified at low temperatures. They pointed out that the lines observed in the solid state correspond to the oscillations of the molecules of *trans* configuration and those observed in the liquid state are due to a mixture of *cis* and *trans* types of molecules. Morino (1938) calculated the frequencies of oscillations of the *trans* configuration of the molecules of these two substances and assigned the frequencies 188 cm^{-1} , 656 cm^{-1} , 1056 cm^{-1} , 1254 cm^{-1} , 1440 cm^{-1} and 2970 cm^{-1} to the six total symmetric oscillations of *trans* ethylene dibromide molecule. Mizushima and Morino (1938a) adduced further evidence in support of this assignment by observing the changes which these frequencies undergo when the hydrogen atoms of the molecule are replaced by deuterium atoms. According to the assignment made by Mizushima and Morino (1938a) all the lines mentioned above should be highly polarised. The polarisation of the Raman lines of ethylene dibromide had been studied by Trumphy (1935) and Anantha Krishnan (1937). According to Trumphy the line 1440 cm^{-1} is completely depolarised while the value of ρ for the line 1056 cm^{-1} was observed by him to be 0.7. According to Anantha Krishnan on the other hand both these lines are completely depolarised. Thus

* Fellow of the Indian Physical Society.

there is a discrepancy between the values of ρ of these two lines actually observed and those expected according to the assignment made by Mizushima and Morino, and this discrepancy was not explained by them. The problem was therefore considered to be worth reinvestigation.

In the present investigation the Raman spectra of ethylene dibromide in the solid state at about -170°C and in the liquid state at the room temperature and the polarisation of the Raman lines of the liquid have been studied. In order to compare the results obtained with ethylene dibromide, which is supposed to consist of a mixture of *cis* and *trans* molecules in the liquid state, with those obtained with a mixture of similar but stable *cis* and *trans* molecules, the Raman spectra of a mixture of *cis* and *trans* dichlorethylene in the solid state at about -170°C and in the liquid state at the room temperature have also been studied.

EXPERIMENTAL

The apparatus used in the present investigation for the study of the Raman spectra at the low temperatures was the same as that used in a previous investigation (Sirkar and Bishui, 1943). Kahlbaum's pure ethylene dibromide distilled in vacuum was put in a double walled cylindrical container of Pyrex glass held in a vertical position inside another transparent Dewar vessel. The interspace between the two walls of the container was evacuated with a Cenco Hyvac oil pump, so that on pouring liquid oxygen into the outer Dewar vessel to fill it up to a certain height from the bottom of the container, the temperature of the liquid was lowered only slowly, and consequently the process of solidification was very slow. The frozen mass thus produced was transparent. Dry air was slowly introduced afterwards into the interspace of the double walled container and the temperature of the solid finally reached a steady value of about -170°C within an hour. A Fuess glass spectrograph having a dispersion of about 14 A.U. per mm. in the region of 4046 Å was used to photograph the Raman spectra. The substance was illuminated by light from two vertical mercury arcs condensed by two glass condensers placed on opposite sides of the container. Cobalt glass filters were placed in the path of the incident rays to cut off continuous background in the blue-green region of the spectrum.

The polarisation of the Raman lines of ethylene dibromide was studied by photographing the horizontal and vertical components of the lines simultaneously on the same plate with the help of a double image prism as usual. The liquid was contained in a horizontal Wood's tube provided with a plane window. Light from a horizontal mercury arc focussed with a glass condenser served as a cone of incident light with its axis perpendicular to that of the Wood's tube. The semivertical angle Ω of the cone of the incident light was about 20° , so that owing to the convergence of the incident beam the apparent value ρ' of factor of depolarisation is given by the relation

$$\rho' = \{\rho + (1-\rho)\psi\} / \{1 - (1-\rho)/2\}\psi \quad \dots (1)$$

where ρ is the real value of the factor of depolarisation, and $\psi = \frac{1}{3}(2 - \cos\Omega - \cos^2\Omega)$ (see Bhagavantam, 1940). When $\rho = 6/7$, $\rho' = 0.94$ in the present case. Owing to the loss of intensity of the vertical component by reflection at the surfaces of the prisms and lenses of the spectrograph the value of ρ' increases still further. Hence lines having ρ' almost equal to unity may be assumed to be totally depolarised under the arrangement mentioned above. This conclusion is further confirmed by the fact that the values of ρ' for some of the highly polarised lines photographed in the same spectrogram along with these depolarised lines were observed to be less than 0.2 which corresponds to a value of ρ equal to 0.05 according to (1).

The Raman spectrum of dichlorethylene (mixture of *cis* and *trans*) in the solid state at about -170°C was studied with the same arrangement as used in the case of solid ethylene dibromide and that of the liquid was also photographed for comparison with the spectrogram due to the solid. The results are discussed in the following section.

RESULTS AND DISCUSSION

The Raman lines observed at different temperatures in the case of ethylene dibromide are listed in Table I. The results obtained by Mizushima and Morino (1938a) in the case of the solid and liquid states of the substance and by Anantha Krishnan (1937) in the case of the liquid state are also included in the table. The numbers in parentheses placed immediately after the wavenumber shifts of the lines indicate approximate relative intensities of the lines and the letters c, k, etc., indicate the exciting lines according to Kohlrausch's notation. The letters P and D indicate that the lines are polarised and totally depolarised respectively.

The results obtained with a mixture of *cis* and *trans* dichlorethylene are given in Table II and those obtained by Cabannes (1938) for pure *cis* and pure *trans* dichlorethylene are also included in the table. In order to understand the nature of changes which the Raman lines of a mixture of *cis* and *trans* types of molecules undergo with the freezing of the mixture we shall first discuss the results obtained with the mixture of *cis* and *trans* dichlorethylene.

DICHLORETHYLENE

It can be seen from columns 1 and 2 of Table II that almost all the Raman lines of the mixture of *cis* and *trans* dichlorethylene in the liquid state are also present in the solid state. The following changes are, however, observed to occur with the solidification of the mixture. The line 563 cm^{-1} which is of moderate intensities in the liquid state becomes very feeble in the solid state. The line 1584 cm^{-1} which is very intense in the liquid state becomes broader and weaker in the solid state. The lines 852 cm^{-1} and 874

TABLE I
Ethylene dibromide

Liquid state			Solid state	
Present authors	Anantha Krishnan (1937)	Mizushima and Morino (1938a)	at -40° C Mizushima and Morino (1938a)	at -170° C Present authors
92 (2b) e, k ; D	92 (2b) D	92 (2b) e ± k ±	41 (4) k ±	35 (3) k
133 (2) e ; ?		132 (2) e	53 (3) k ±	52 (2) k
196 (8) e ±, k - ; P	189 (10) P	190 (10) e ±, k ±	v	125 (1) e, k
232 (2) e ; P	228 (1b) P	231 (3) e	187 (7) e + k +	188 (6) e, k
325 (0) e ; ?	320 (0) ?	325 (1) e	v	
354 (3) e ; D	358 (2) D	355 (5) e, k	v	
470 (1) e, k ; ?	470 (0) ?	469 (1) e, k		
551 (7) e ±, k, i ; P	551 (8) PP	551 (8) e ±, l, g, i, k	v	
582 (4b) e, k, i ; D	580 (2b) D	583 (6b) e ±, k, i	v	581 (0) k
660 (10b) e, k, i ; P	659 (15b) P	660 (10b) e ±, k, i	656 (10) e, k, i, f, g	656 (10) e, k, i, f
	790 (0) ?			
836 (2) e ; D	834 (½) D	836 (2) e		
832 (2) e, k ; P	895 (1) P	899 (3) e, k		
935 (0) e, k ; ?	930 (1b) P (?)	930 (2) e, k	933 (0) k	
		1019 (1) e, k		
1052 (8) e, k, i ; D	1051 (6) D	1053 (9) e, k, i	1056 (5) e, k, i	1056 (5) e, k, i
1170 (2) e, k ; D	1169 (½) D	1169 (3) e, k	1157 (1) e	
1258 (10b) e, k ; P	1256 (10b) P	1255 (10b) e, k	1254 (8) e, k, i	1254 (8) e, k
	1295 (18) P	1276 (3) e, k	v	
1421 (2) e, k ; D	1419 (1) D	1419 (3) e, k	b	
1438 (4) e, k ; D	1436 (2) D	1440 (5) e, k	1436 (3) e, k	1435 (2) e, k
2837 (3) e, k ; P	2852 (1) PP	2859 (4) e, k	2848 (2) e, k	2848 (0)
2950 (8) e, k, i ; P	2950 (6) PP	2953 (8) e, k, i	v	
2975 (10b) e, k, i ; P	2970 (8) PP	2972 (10) e, k, i	2968 (8) e, k, i	2971 (7) e, k
3012 (4b) e ; D	3012 (2b) D	3013 (4b) e, (k)	3020 (2) e, (k)	3017 (1) e

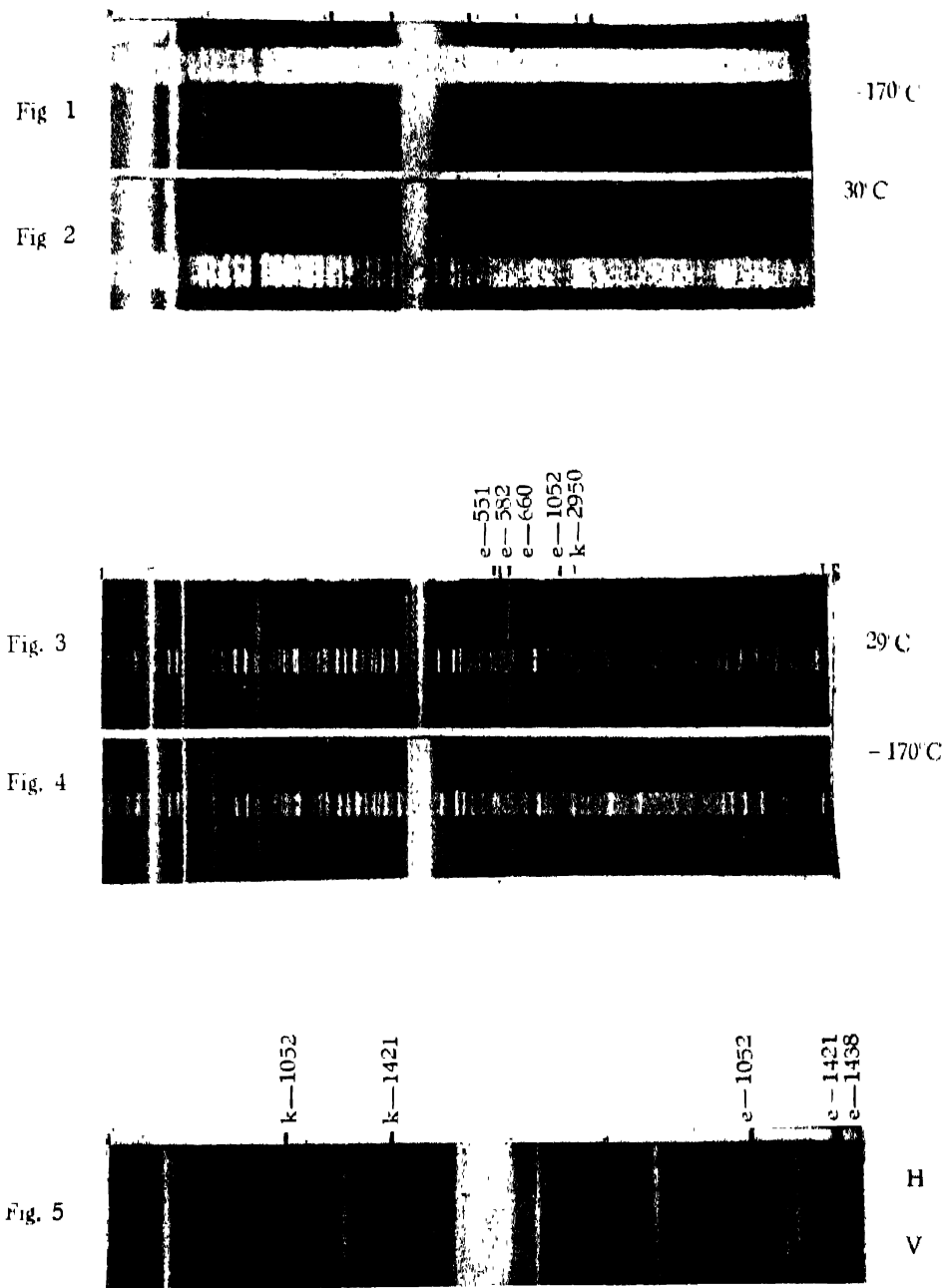
TABLE II
1, 2-Dichloroethylene

Present authors		Cabannes (1938)	
Liquid (mixture of cis and trans)	Solid at -170° C	Liquid (cis)	Liquid (trans)
	60 (2b) k		
171 (8) e, k	173 (3b) e	^p	^p
351 (5) e, i	360 (3b) e	174 (16) 0.52	351 (20) 0.29
407 (5) e	410 (2b) e	406 (10) 0.85	
563 (4) e, k	567 (0) e	564 (6) 0.89	
712 (10) e, i, k	712 (4b) e, k	711 (20) 0.66	766 (4) 0.70
760 (2) e, k	760 (0) e	809 (1) P	
852 (3) e, k	860 (1) e	875 (2) D	848 (7) 0.09
874 (3) e, k		1179 (12) 0.69	
1179 (10) e, i, k	1180 (3) e, k	1586 (16) 0.19	1271 (14) 0.21
1274 (5) e, k	1274 (1) e	1688 (4) P	1576 (11) 0.10
			1630 (½) P
1584 (20) e, k	1584 (4b) e, k	3077 (20) 0.27	1693 (1) P
1695 (3) e			3070 (12) 0.20
3075 (20) e, k, q	3082 (6b) e, k	3178 (2) D	3142 (2) D ?
3170 (2) e, k	3170 (0) k		

cm^{-1} observed in the liquid state coalesce to form a broad line at 860 cm^{-1} in the solid state. The lines 351 cm^{-1} , 407 cm^{-1} and 3075 cm^{-1} also undergo slight changes in position with the solidification of the substance and a new band at 60 cm^{-1} is observed in the solid state. The spectrograms are reproduced in Plate I (Figs. 1 and 2).

Most of the lines observed in the liquid state have been assigned by Cabannes (1938) to the particular modes of vibration of the *cis* and *trans* types of the molecule. The *trans* configuration of the molecule has the symmetry of the point group C_{2h} and has according to group theory five total symmetric and one antisymmetric oscillations allowed in Raman effect. The five polarised lines 351 cm^{-1} , 848 cm^{-1} , 1271 cm^{-1} , 1576 cm^{-1} and 3070 cm^{-1} are assigned to the total symmetric oscillations, and of these the most intense lines 351 cm^{-1} and 1271 cm^{-1} are supposed to be due to the deformation oscillations of the C-Cl and C-H bonds respectively. According to Cabannes the Raman line due to the mode of oscillation antisymmetric to the plane of the molecule is too weak to be observed and the line 766 cm^{-1} is not identified with this oscillation, because it is not totally depolarised, the value of ρ being 0.7 and definitely less than 6/7. This line is supposed to be an overtone of the deformation oscillation antisymmetric to the centre of symmetry, the fundamental being forbidden in Raman effect.

In the case of the *cis* configuration of dichloroethylene which has the symmetry C_{2v} five total symmetric and seven antisymmetric oscillations are allowed in the Raman effect according to the group theory. The five total symmetric modes are identified by Cabannes (1938) with the lines 174 cm^{-1} , 712 cm^{-1} , 1179 cm^{-1} , 1586 cm^{-1} and 3077 cm^{-1} which are all polarised. Of the seven totally depolarised lines expected from the theory only four are actually observed. These are 406 cm^{-1} , 564 cm^{-1} , 875 cm^{-1} and 3178 cm^{-1} . The last one is, however, assumed by Cabannes to be due to an overtone of 1586 cm^{-1} , but this assumption is not justified, because the line is totally depolarised while all overtone modes should give polarised Raman lines. Again, the line 1688 cm^{-1} is assumed by him to be an overtone of 875 cm^{-1} but since both these lines are almost equally intense, one of them cannot be the overtone of the other. In the mixture of *cis* and *trans* dichloroethylene in the liquid state only a single line at 1695 cm^{-1} is observed in the present investigation in place of the three lines 1630 cm^{-1} , 1688 cm^{-1} and 1693 cm^{-1} due to the two constituents and the line is too weak to be observed in the solid state. Also another line at 3170 cm^{-1} is observed in place of the lines 3142 cm^{-1} and 3178 cm^{-1} observed by Cabannes in the case of *cis* and *trans* configurations respectively. These facts indicate the influence of van der Waals forces on the frequencies of the corresponding vibrations. Probably some sort of association disturbs slightly the centre of symmetry of pure *trans* dichloroethylene molecule in the liquid state and when mixed with the *cis* type this symmetry is restored. The line 3142 cm^{-1} is probably due to the antisymmetric C-H valence oscillation and it has thus a feeble intensity in the pure state and disappears in the



Raman Spectra

- Fig. 1 Dichlorethylene, solid at -170°C
- Fig. 2 " " liquid " -30°C
- Fig. 3 Ethylene dibromide liquid at -29°C
- Fig. 4 " " solid " -170°C
- Fig. 5 " " liquid, polarisation

mixture because of restoration of the centre symmetry of the molecule. The new line at 60 cm^{-1} is due to some intermolecular oscillation, because the single molecule cannot have any mode of vibration of such a low frequency. The line is broad and feeble and it is difficult to say whether it is due to pure lattice oscillation or due to some vibration in associated molecules.

It is therefore seen from the above discussions that in the case of both *cis* and *trans* molecules all the total symmetric oscillations yield intense Raman lines and the antisymmetric oscillation in the case of the *trans* type as well as some of similar oscillations in the case of the *cis* type are absent in the Raman spectra.

ETHYLENE DIBROMIDE

It can be seen from Table I that many of the lines observed in the case of liquid ethylene dibromide are absent in the solid state at the low temperature. This can also be seen from the spectrograms reproduced in Plate I (Figs. 3 and 4). The results are in general agreement with those reported by Mizushima and Morino (1938a), but there are a few minor discrepancies. The lines 581 cm^{-1} does not disappear completely in the solid state at -170°C , but it becomes definitely much feebler in the solid state. This statement is based on the fact that a very weak Raman line at $\lambda\ 4143.8$ has been observed in the present investigation in the case of the solid state at -170°C , although Mizushima and Morino did not record any such line in the case of the solid at -40°C . The Raman line 551 cm^{-1} excited by $\lambda\ 4358$ almost coincides with the line 656 cm^{-1} excited by $\lambda\ 4339$ and the same line excited by $\lambda\ 4047$ coincides with the Hg line $\lambda\ 4140$. Hence although a faint line is actually observed at $\lambda\ 4466.5$ it cannot be said definitely whether it is solely the line 656 cm^{-1} excited by $\lambda\ 4339$ or the line 551 cm^{-1} excited by $\lambda\ 4358$ is also superposed on it with a very feeble intensity. It can, however, be stated with certainty that even if the line 551 cm^{-1} be superposed on the line 656 cm^{-1} excited by $\lambda\ 4339$ the intensity of the former line is almost negligible in the solid state in comparison with that in the liquid state.

The lines 933 cm^{-1} and 1157 cm^{-1} observed by Mizushima and Morino (1938a) at -40°C have not been observed in the spectrogram due to the solid at -170°C obtained in the present investigation, but a line at 125 cm^{-1} observed in this spectrogram has not been observed by them at -40°C . The results regarding polarisation of the Raman lines of the liquid obtained in the present investigation agree with those reported by Anantha Krishnan (1937). According to these results the lines 1056 cm^{-1} and 1440 cm^{-1} are totally depolarised. It is difficult to reconcile this fact with the assignment made by Mizushima and Morino (1938a) that these lines are due respectively to the total symmetric C-C valence and C-H deformation oscillations of the single molecule of *trans* configuration, because we have already seen that in the case of similar molecule of *trans* dichlorethylene the corresponding Raman lines are observed to be polarised and they appear with undiminished intensity in the solid state.

According to Mizushima and Morino the solid state of the substance consists entirely of single molecules of trans configuration. This molecule has six total symmetric and three antisymmetric modes of oscillation allowed in Raman effect according to the group theory. The fact that more than nine lines are observed in the solid state and of the six lines which are expected to be polarised two are totally depolarised, probably indicates that the solid state consists not of single molecules but of larger molecules formed by association of single molecules. The line 92 cm^{-1} observed in the case of the liquid state cannot be due to any mode of oscillation of the single molecule, and Mizushima and Morino (1938b) have pointed out that this line may originate from some oscillation of the conglomerate of molecules, such conglomerates being present only in the liquid state. It is, however, difficult to believe that if conglomerates are present in the liquid state they can dissociate into single molecules in the solid state. On the contrary, there is every possibility of the strengthening of the intermolecular bonds in such conglomerates with the solidification of the substance. The two new lines 41 cm^{-1} and 53 cm^{-1} observed in the solid state may also be due to some vibration in such associated groups of the molecules. All these facts indicate that we may have to assume that solid ethylene dibromide consists of associated pairs of molecules. An attempt will be made now to explain the polarisation of the Raman lines of the liquid on the basis of this assumption. It has to be pointed out, however, that the polarisation of the lines in solid state may not be the same as that of the corresponding lines in the liquid state.

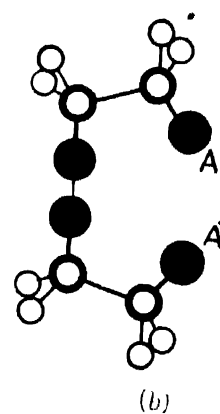
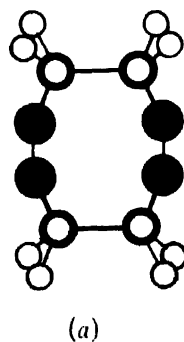
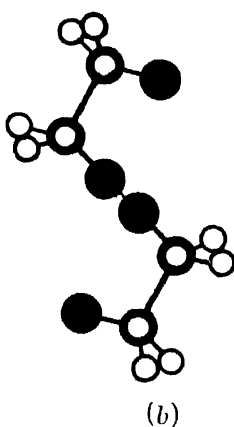
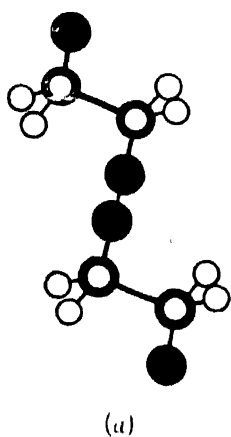


FIG. 6

FIG. 7

If two molecules of ethylene dibromide become associated by some virtual bond between two bromine atoms one belonging to each molecule, we can have two different configurations as shown in figures 6 and 7. The configuration shown in figure 6 is centrosymmetrical and may be formed by two molecules, both being either of *cis* or of *trans* type. The symmetry of the configuration is C_{2h} . The character table of this point group as well as the number of Raman lines allowed for the configuration are given in Table III in which n_i denotes the total number of times the particular irreducible representation is contained in the reducible representation and n'_i , the number of oscillations represented by

the irreducible representations excluding pure translations and pure rotations. The number of Raman lines allowed are given in the column under "Raman effect" and the nature of polarisation of the lines is also indicated in the last column by the letters P and D.

TABLE III
Symmetry C_{2h}

	E	C_2	σ_h	i	n_r	T & R	n_r	Raman effect	Polarisation
Γ_1	1	1	1	1	14	1	13	13	P
Γ_2	1	-1	-1	1	10	2	8	8	D
Γ_3	1	1	-1	-1	10	1	0	f	—
Γ_4	1	-1	1	-1	14	2	11	f	—
U_R	16	0	8	0	21 Raman lines				
$h_x x'_j$	48	0	8	0					
$h_y y'_j$	42	2	8	0					

The other configuration is formed by two molecules of the *cis* type as shown in figure 7(a) and has the symmetry D_{2h} . The corresponding character table is included in Table IV.

TABLE IV
Symmetry D_{2h}

	E	C_2	C_2'	C_2''	σ_h	σ_v	σ_v'	i	n_r	T&R	n_r	Raman effect	Polarisation
Γ_1	1	1	1	1	1	1	1	1	7	0	7	7	P
Γ_2	1	1	-1	-1	1	1	-1	-1	7	1	6	f	—
Γ_3	1	-1	1	-1	1	-1	1	1	7	1	6	f	—
Γ_4	1	-1	-1	1	1	-1	-1	1	7	1	6	6	D
Γ_5	1	1	1	1	-1	-1	-1	-1	5	0	5	f	—
Γ_6	1	1	-1	-1	-1	-1	1	1	5	1	4	4	D
Γ_7	1	-1	1	-1	-1	1	-1	1	5	1	4	4	D
Γ_8	1	-1	-1	1	-1	1	1	-1	5	1	4	f	—
U_R	16	0	0	0	8	0	0	0	21 Raman lines				
$h_x x'_j$	48	0	0	0	8	0	0	0					
$h_y y'_j$	42	2	2	2	8	0	0	0					

It can be seen from the Tables III and IV that both the configurations yield the same number of Raman lines, but in the case of that shown in figure 6, thirteen of the twenty one Raman lines are polarised and the remaining eight are totally depolarised. In the case of the other configuration shown in figure 7(a) there should be seven polarised and fourteen depolarised Raman lines. It has been observed in the case of *cis* and *trans* dichloroethylene that most of the depolarised Raman lines are either feeble or absent. Since we do not observe more than twelve lines in the Raman spectrum of solid ethylene dibromide any of the configurations shown in figure 6 cannot be supposed to be responsible for the origin of these Raman lines, because such a configuration ought to have given thirteen polarised Raman lines. We can, however, explain the origin of

the observed Raman lines by assuming that they are due to the configuration shown in figure 7(a) and that seven of the twelve Raman lines observed in the solid state are polarised and five are depolarised. The remaining depolarised lines may be too feeble to be observed, as in the case of dichlorethylene.

In the case of the liquid state the virtual bond between one of the two pairs of bromine atoms may be absent thus producing a configuration having a symmetry C_{2v} as shown in fig. 7(b). This should yield forty two Raman lines of which thirteen should be polarised and the rest depolarised. The maximum number of lines observed in the liquid state is twenty-four and of these nine are definitely polarised and three of these polarised lines being broad, each may consist of two lines. Thus almost all the polarised lines expected for the configuration indicated above are actually observed. As regards the depolarised lines ten definitely depolarised lines are observed of which three are broad and there are three more faint lines which also may be depolarised. This may account for altogether sixteen out of twenty-nine depolarised lines expected. Some of the depolarised lines should be absent as observed in the case of *cis* and *trans* dichlorethylene. According to the hypothesis put forward by Mizushima and Morino that the liquid may consist of a mixture of *cis* and *trans* molecules we shall also expect twelve polarised and fifteen depolarised Raman lines in the case of the liquid state. But the present hypothesis has the following advantages over that put forward by them. :

(a) According to the present hypothesis the line 1051 cm^{-1} due to the liquid may be totally depolarised, because it can be identified with the C-C valence oscillation antisymmetric to the plane of reflection possessed by the associated pair of molecules having the symmetry C_{2v} , but according to the previous hypothesis the line ought to have been polarised although it is actually not so. The line 1056 cm^{-1} observed in the solid state may be due to the symmetric C-C valence oscillation of the model shown in figure 7(a).

(b) The lines of frequencies less than 190 cm^{-1} cannot originate from any mode of oscillation of either *cis* or *trans* ethylene dibromide molecules and so according to the previous hypothesis conglomerates of molecules were postulated to be present in the liquid state and absent in the solid state. The present hypothesis can explain the origin of these lines by assuming that they are due to oscillations of associated pair of molecules present both in the solid and liquid states.

(c) In order to explain the behaviour of the new lines in the low frequency region observed in the solid state Mizushima and Morino (1938b) assumed that the molecules of ethylene dichloride can rotate freely about the Cl-C-C-Cl axis above -95°C , although the rotation about the C-C bond is stopped by freezing the substance. In the explanation offered in the present paper no such assumption, which seems to be hardly tenable, has been made. The lines in the low frequency region may be due to some oscillations of the pair of molecules as stated before.

Besides explaining the discrepancies between the observed facts and the predictions of the hypothesis put forward by the previous authors mentioned

above, the configurations of pairs of molecules assumed to be present in the liquid and solid states of ethylene dihalides can also explain the permanent electric moments of the molecules observed in the two states. The configuration of the pair having the symmetry C_{2v} will possess a permanent electric moment and that present in the solid state and possessing the symmetry D_{2h} should have no electric moment, as observed by White and Morgan (1937).

The gradual diminution in the observed value of the permanent electric moment of the molecule with the lowering of the temperature may be due to the gradual diminution in the distance between the two bromide atoms marked A A' in configuration shown in figure 7(b). As the temperature is lowered probably the opening in the ring is gradually narrowed down and finally the gap is closed, and the configuration becomes a centro-symmetrical one with the solidification of the substance. With the approach of the symmetry of the configuration to the centro-symmetrical one there is a diminution in the change in polarisability of the molecule taking place during some modes of oscillations which become antisymmetric to centre of symmetry in the case of the centro-symmetrical configuration. Thus the weakening of the intensity of some of the Raman lines, e.g., the lines 551 cm^{-1} and 581 cm^{-1} and 2050 cm^{-1} with the lowering of the temperature can be explained.

Attempts to explain on these lines the results observed with other similar molecules will be made in later communications.

ACKNOWLEDGMENT

The authors are indebted to the authorities of the Indian Association for the Cultivation of Science for providing facilities for carrying out the experimental portion of the investigation in the Laboratories of the Association and for the award of a scholarship to one (B. M. B.) of them.

PHYSICS DEPARTMENT
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA.

REFERENCES

- Anantha Krishnan, R., 1937, The Raman Spectra of some simple molecules, *Proc. Ind. Acad. Sc. A.*, **5**, 285.
Bhagavantam, S., 1940, *Scattering of light and the Raman Effect*, p. 303.
Cabannes, J., 1938, The *cis trans* Isomerism, *J. Chimie Physique*, **36**, 1.
Mizushima, S. and Morino, Y. 1938a, Raman Spectra and molecular configurations of solid ethylene dihalides, *Proc. Ind. Acad. Sc. A.*, **8**, 315.
Mizushima, S. and Morino, Y., 1938b, The motion of ethylene halide molecules in crystals, *Bull. Chem. Soc., Japan*, **13**, 182.
Mizushima, S. Morino, Y. and Noziri, 1936, Raman Effect and free rotation, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, **29**, 63 and 188.
Morino, Y., 1938, The normal vibrations of ethylene halides, *Bull. Chem. Soc., Japan*, **13**, 189.
Sirkar, S. C. and Bishui, B. M., 1943, Raman Spectra of some Alkyl sulphides in the solid state, *Proc. Nat. Inst. Sc.*, **9**, 287.
Trumpy, B., 1936, Polarisation of Raman lines, *Z. f. Phys.*, **98**, 672.
White and Morgan, 1937, *J. Chem. Phys.*, **5**, 655