The Motion of Ethylene Halide Molecules in Crystals as Revealed by the Raman Effect.

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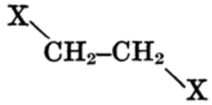
The conspicuous difference in the Raman spectra of ethylene dihalides between the liquid and solid states reported in our previous paper was explained as due to the considerable change of the intramolecular state upon solidification.(1)(2) Below the freezing point the molecules are almost all in the *trans* configuration  $\overset{X\diagdown}{}CH_2\text{–}CH_2\underset{\diagdown X}{}$, while in the liquid state or in solutions there is a considerable deviation of the mean internal state from this stable position. (It was shown by our calculation(2) of normal vibrations that the Raman lines observed in the solid state all correspond to the symmetric vibrations to the centre of symmetry of the *trans* form.) The sharp drop of dielectric constant of ethylene chloride and bromide at the freezing point recently observed by White and Morgan is in conformity with our conclusion, which is discussed fully in their communication.(3)

In the vicinity of the unmodified line there seemed to exist other Raman lines which we could not resolve from the primary line in our former measurement. As it is doubtless important for the investigation of intermolecular state to confirm the existence of such low frequency lines, we have reexamined the Raman spectra of ethylene chloride and bromide with a spectrograph of our own construction having a larger dispersion and higher luminocity than the former one (dispersion 10 Å/mm. at 4000 Å). As was expected we could really observe fairly intense Raman lines in the said frequency region both as Stokes and anti-Stokes—for ethylene chloride at −40°C. a diffuse line was observed at 66 $cm.^{-1}$, and for ethylene bromide at 0°C. a line of the same nature at 49 $cm.^{-1}$, while for the latter substance at −40°C. two sharp and fairly intense lines appeared at 41 and 53 $cm.^{-1}$ respectively (see Figs. 1 and 2).

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(1) Mizushima, Morino, and Noziri, *Nature*, **137** (1936), 945.

(2) Mizushima, Morino, and Noziri, *Sci. Papers Inst. Phys.-Chem. Research* (Tokyo), **29** (1936), 63.

(3) White and Morgan, *J. Chem. Phys.*, **5** (1937), 655.

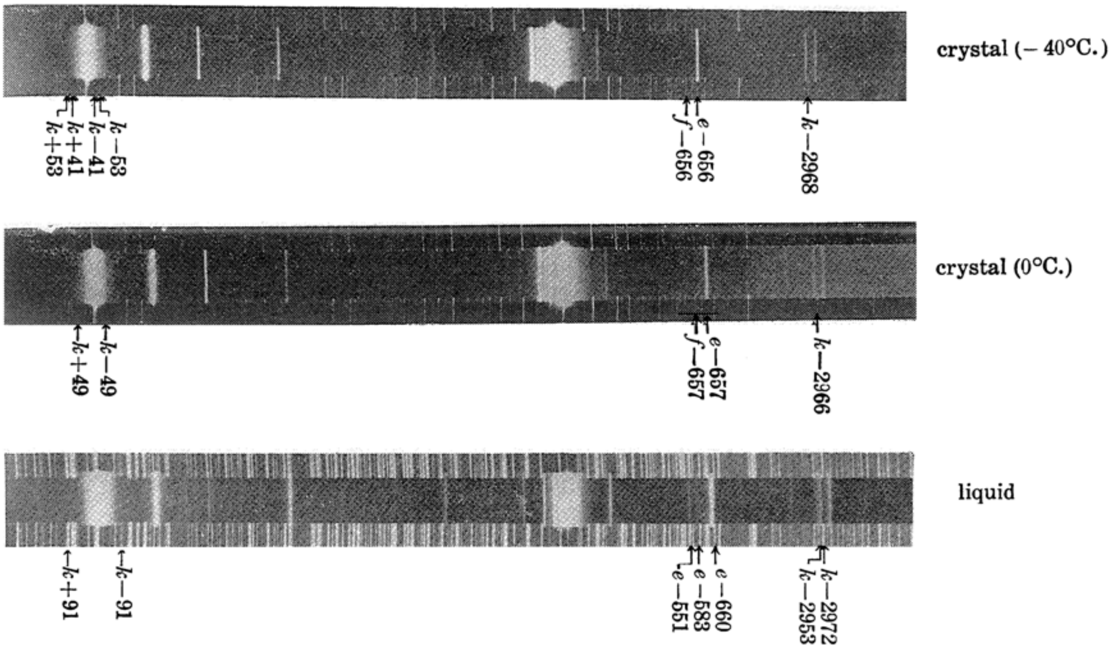

Fig. 1. Raman spectra of ethylene bromide.

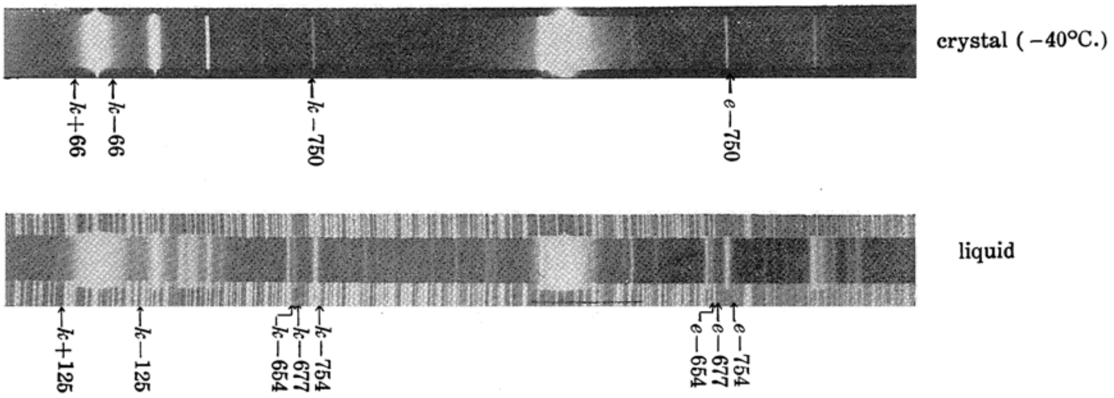

Fig. 2. Raman spectra of ethylene chloride.

It is very interesting to consider the observed change in Raman spectrum of the crystalline ethylene bromide in connection with the thermal transition observed at −24°C. by White and Morgan,(3) from which it may be concluded that these low frequency lines correspond to some motion of a molecule as a whole in the crystal lattice. There are two more reasons which would justify this conclusion: (1) we could observe no line (at least of the comparable intensity) in this frequency region of the liquid spectra, (2) the frequencies of these lines are too low to be identified with any of the internal normal vibrations,(4) as can be seen from our calculation for these molecules.(2)

Let us tentatively assume that these low frequency lines correspond to lattice frequencies and see how far we can treat our interesting experimental results with this assumption. In these crystals the van der Waals force between the halogen atoms would play the leading part in forming the molecular lattice, because of the greater polarizability of these atoms. This is also in conformity with the appearance of these lattice frequencies as the Raman effect, since there can also take place a considerable change in polarizability for the lattice vibration in such a crystal.

Before entering into the detailed discussion of this problem, we have to consider somewhat about the intramolecular state as revealed by the lines of higher frequencies. The values of Raman frequencies observed in the present experiment are no doubt of greater precision than those reported in our previous communication because of the larger dispersion of the spectrograph used. As far as, however, the conclusion given previously(2) is concerned, nothing need be changed. The disappearance of some of the liquid lines in the solid spectrum, which was the most important result of our previous experiment, has acquired further confirmation by the high luminocity of the present apparatus,—e.g. in the solid spectra we could observe distinctly the Raman lines excited by Hg-*f* and Hg-*g*, which correspond to the symmetric C–X vibrations (750 cm.$^{-1}$ for $C_2H_4Cl_2$ and 656 cm.$^{-1}$ for $C_2H_4Br_2$), but could find no trace of strong liquid lines to be found in their vicinity even by Hg-*e* excitation (654 cm.$^{-1}$ for $C_2H_4Cl_2$ and 551 cm.$^{-1}$ for $C_2H_4Br_2$). Thus it is quite sure that below the freezing point the molecule of ethylene halide is in a nearly pure *trans* state and the thermal transition observed for ethylene bromide at −24°C. has no effect on this intramolecular configuration.

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(4) The intramolecular oscillatory rotation about the *trans* position (compare footnote (5)), which can have a frequency value of this order of magnitude, is not allowed in the Raman effect for the solid state, since this normal vibration is antisymmetric to the centre of symmetry of the *trans* configuration.

Returning to the problem of intermolecular motion, let us consider that the change in Raman spectrum of crystalline ethylene bromide is caused by the transition observed at −24°C. Then the said change of Raman lines must be due to the change in the molecular lattice. Now many thermal transitions are doubtless caused by the setting-in of molecular rotation in the crystal lattice, for which Pauling⁽⁵⁾ first gave a theoretical treatment. The transition observed for ethylene bromide cannot, however, correspond to the onset of three dimensional molecular rotation in the crystal lattice, as can easily be seen from the following discussion. We have already stated that upon solidification the intramolecular rotation about the C–C axis is greatly restricted and the molecule assumes practically the pure *trans* form. This must be explained in terms of crystal forces. Such a specific effect of these forces in fixing the shape of the molecule would not be expected, if it were rotating about three axes. Taking into account our former result in Raman measurement,⁽¹⁾ White and Morgan explained the thermal transition of ethylene bromide observed by them as due to the onset of molecular rotation about only one axis, i.e. that of the zigzag Br–C–C–Br chain. Rotation about this axis does not contradict the existence of the said crystal forces which keep the molecules of the solid in a nearly pure *trans* state and it would not require a large amount of energy which is consistent with the small value of heat of transition estimated by White and Morgan.⁽³⁾ The commencement of such a molecular rotation necessarily causes a change in the molecular field in the crystal lattice which affects the value of force constant and consequently the frequency of a normal vibration. The small frequency shifts observed for some of the lines of crystalline ethylene bromide (see Table 1) might be interpreted as due to such a change in the molecular field on passing through the transition point. That we have found no appreciable change in frequency on fusion (see Table 1), would then be of particular interest, when we consider that the molecules are rotating in the liquid state as well as in the solid state above the transition point. The experimental error in the reading of each line is different according to the character of the line and consequently

Table 1. Frequency changes in some of the high frequency lines of ethylene bromide.

Crystal		Liquid
−40°C.	0°C.	
2848	2857	2859
3020	3013	3013

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(5) Pauling, *Phys. Rev.*, **36** (1930), 430; see also Smyth, *Chem. Rev.*, **19** (1936), 329.

we cannot treat these small frequency shifts for all lines with the same accuracy, although the complete treatment would be desirable from the view-point of the modern theory of the liquid state (quasi-crystalline structure). In this connection we want to mention the existence of a very diffuse line of the frequency of 91 cm.$^{-1}$ observed in the liquid spectrum. At the present stage we cannot conclude that this line corresponds to the line of 49 cm.$^{-1}$ observed for the solid at 0°C., indicating the quasi-crystalline structure of the liquid. It is also probable that this line corresponds e.g. to the intermolecular vibration of a conglomerate of molecules existing only in the liquid state. In any case this line has frequency too low to be indentified with any of the internal vibration of ethylene bromide molecule as can easily be seen from our previous calculation.(2)

The spectrum of crystalline ethylene chloride at -40°C. has only one Raman line in the region of the unmodified line and the nature of this line is similar to that of the corresponding line of crystalline ethylene bromide at 0°C. Moreover, on fusion there have been observed no appreciable frequency shifts of the two hydrogen vibrations (2874 cm.$^{-1}$ of solid to 2874 cm.$^{-1}$ of liquid and 3005 cm.$^{-1}$ of solid to 3004 cm.$^{-1}$ of liquid) corresponding to the two bromide lines discussed above. These may suggest that the molecule of ethylene chloride exerts one dimensional rotation around the axis of the zigzag Cl–C–C–Cl chain at this temperature and also at considerably lower temperatures, since there was found no transition point in the thermal measurement by White and Morgan down to -95°C. We have then to consider that the potential hump restraining the said one dimensional rotation in the crystal is smaller for ethylene chloride than for ethylene bromide and the molecules of the former substance can exert rotation at lower temperatures than those of the latter.

One might doubt if the thermal energy at -95°C. can give rise molecular rotation for ethylene chloride, while it cannot cause rotation for ethylene bromide below -24°C. The alternative possibility is that the molecules of ethylene chloride are fixed in the lattice or performing only the oscillatory rotation around the equilibrium orientations (this should not be confused with the intramolecular oscillatory rotation with which we have been dealing(6)). It is conceivable that because of the difference in size between chlorine and bromine atoms the potential hump acting against the one dimensional rotation becomes so large in the crystal of ethylene chloride as to permit no rotation below the freezing point. It is obviously too early at the present stage to give decision between these

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(6) Mizushima, Morino, and co-workers, *Physik. Z.*, **35** (1934), 905; **36** (1935), 600; **38** (1937), 459; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; **26** (1934), 1; **29** (1936), 63, 111, 188; **31** (1937), 296; **32** (1937), 33, 129, 220.

two alternative possibilities. The investigation of the Raman spectrum of ethylene iodide, which we have already begun, might throw light on this problem.

We have no intention of giving here a conclusive explanation for our experimental result. The object of the present paper is to report these very interesting observations and to suggest a probable explanation for them.

Experimental.

In the present investigation we used a spectrograph of higher luminocity and a mercury lamp of stronger radiation than in our previous measurement. This together with the use of Agfa Isopan ISS film considerably reduced the time of exposure. For the crystals the longest exposure in the present experiment amounted to 15 hours, which would correspond to an exposure of more than two hundred hours with our previous apparatus. In order to investigate the region of the unmodified line, it is important to avoid as much as possible all parasitic light and stray reflections from the face of the crystals. This condition was secured by using carefully distilled liquids, which was allowed to solidify to a uniform mass. As the filters we have used, according to the suggestion of Ananthakrishnan,(7) dilute as well as con-

Table 2. The Raman spectra of $C_2H_4Cl_2$.

Solid state (−40°C.)			Liquid state					
			Present authors			Ananthakrishnan		
66	(4b)	*k*±						
	v		125	(5b)	*e*±, *k*±	123	(4b)	D
	v		265	(5)	*e*±, *k*, *i*	263	(2)	P
302	(5)	*e*, *k*	300	(8)	*e*±, *k*, *i*	302	(8)	P
	v		411	(5)	*e*±, *k*, *i*	411	(3)	D
	v		654	(8)	*e*±, *k*, *i*, *f*	654	(10)	PP
	v		677	(6b)	*e*±, *k*, *i*	675	(3)	D
750	(10)	*e*, *k*, *i*, *f*	754	(10b)	*e*±, *k*, *i*	754	(15b)	P
	v		881	(4)	*e*, *k*	880	(1)	D
	v		943	(5)	*e*, [*k*]	940	(2)	P
992	(3)	*e*, *k*	989	(2)	*e*, *k*			
			1031	(2)	*e*, *k*			
1059	(3)	*e*, *k*	1052	(4)	*e*, *k*	1052	(1)	P
			1145	(3)	*e*, *k*	1144	($^1/_2$)	D
	v		1207	(5)	*e*, *k*	1206	(2)	D
1265	(2b)	*k*	1264	(3)	*e*, *k*	1262	(1)	D
1301	(5b)	*k*	1304	(6)	*e*, *k*	1302	(3)	P
			1393	(1)	*e*, *k*			
	v		1429	(6)	*e*, *k*	1429	(3)	D
1448	(2b)	*e*, *k*	1445	(4b)	*e*, *k*	1440	($^1/_2$)	D
			2844	(3)	*e*, *k*	2844	(1)	?
2874	(3)	*e*, *k*, *i*	2874	(4)	*e*, *k*	2872	(1)	P
2964	(10)	*e*, *k*, *i*	2957	(10)	*e*, *k*, *i*	2956	(12b)	PP
3005	(6)	*e*, *k*, *i*	3004	(8b)	*e*, *k*, *i*	3002	(4b)	D

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(7) Ananthakrishnan, *Proc. Indian Acad. Sci.*, A, **5** (1937), 76.

centrated solutions of iodine in carbon tetrachloride, which proved to be quite useful for our present purpose.

The results of our Raman measurement are shown in Tables 2 and 3, in which there is listed for each observed line: first, its frequency in cm.$^{-1}$; second, in parenthesis, its intensity as obtained by visual estimation; third, the mercury lines exciting it. The letter b following the number indicating the intensity, signifies a broad line and v in the columns of the solid spectra means the disappearance of the corresponding liquid line undoubtedly established in the accuracy of the present measurement. For the sake of comparison the experimental values of Ananthakrishnan(8) obtained for liquid ethylene chloride and bromide are inserted in the following tables.

Table 3. The Raman spectra of $C_2H_4Br_2$.

Solid state (−40°C.)	Solid state (0°C.)	Liquid state	
		Present authors	Ananthakrishnan
41 (4) *k*±	49 (3b) *k*±		
53 (3) *k*±			
v	v	91 (2b) *e*±, *k*±	92 (2b)
		132 (2) *e*	
187 (7) *e*±, *k*+	190 (7) *e*, *k*+	190 (10) *e*±, *k*±	189 (10) P
v	v	231 (3) *e*	228 (1b) P
		325 (1) *e*	320 (0) ?
v	v	355 (5) *e*, *k*	358 (2) D
		469 (1) *e*, *k*	470 (0) ?
v	v	551 (9) *e*±, *k*, *i*, *f*	551 (8) PP
v	v	583 (6b) *e*±, *k*, *i*	580 (2b) D
656 (10) *e*, *k*, *i*, *f*, *g*	657 (10) *e*, *k*, *i*, *f*	660 (10b) *e*±, *k*, *i*	659 (15b) P
			790 (0) ?
		836 (2) *e*	834 ($^1/_2$) D
		899 (3) *e*, *k*	895 (1) P
933 (0) *k*	934 (1) *k*	933 (2) *e*, *k*	930 (1b) P
		997 (0) *e*	
		1019 (1) *e*, *k*	
1057 (5) *e*, *k*, *i*	1056 (5) *e*, *k*	1053 (9) *e*, *k*, *i*	1051 (6) D
			1086 (??)
1157 (1) *e*		1169 (3) *e*, *k*	1169 ($^1/_2$) D
			1187 (0) D
1254 (8) *e*, *k*, *i*	1250 (8b) *e*, *k*	1255 (10b) *e*, *k*	1256 (10b) P
v	v	1276 (8) *e*, *k*	1295 (1s) P
v	v	1419 (3) *e*, *k*	1419 (1) D
1436 (3) [*e*], *k*	1438 (3) [*e*], *k*	1440 (5) *e*, *k*	1436 (2) D
2848 (2) *e*, *k*	2857 (3) *e*, *k*	2859 (4) *e*, *k*	2852 (1) PP
v	v	2953 (8) *e*, *k*, *i*	2950 (6) PP
2968 (8) *e*, *k*, *i*	2966 (10) *e*, *k*, *i*	2972 (10) *e*, *k*, *i*	2970 (8) PP
3020 (2) *e*, [*k*]	3013 (5) *e*, *k*, *i*	3013 (4b) *e*, [*k*]	3012 (2b) D

We thank Prof. M. Katayama and Prof. I. Nitta for their valuable advices. We are indebted to Hattori-Hôkôkai for a grant in aid of this research.

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(8) Ananthakrishnan, *Proc. Indian Acad. Sci.*, A, **5** (1937), 285.

Summary.

In the region of the unmodified line there have been observed for crystalline ethylene halides some Raman lines which correspond to motions of a molecule as a whole, but not to internal normal vibrations. For ethylene bromide a considerable change in these low frequency lines was observed between the spectrum at −40°C. and that at 0°C. and it is highly probable that this change is caused at the transition temperature (−24°C.) observed in the thermal measurement. An explanation for these experimental results was suggested to identify these lines with lattice frequencies and to regard the transition point as the temperature at which the one dimensional molecular rotation sets in.

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