ON THE RAMAN SPECTRA OF DIFFERENT MODIFICATIONS OF A FEW CRYSTALS.

By S. C. SIRKAR

AND

J. GUPTA

ABSTRACT.—The Raman spectra of different modifications of crystals of p-dichlorobenzene, p-dibromobenzene and sulphur have been studied at different temperatures including that of liquid air. It has been observed that in the case of the last two of the above substances no abrupt change takes place with the transformation from one modification to the other in the positions of the new lines which appear in the case of the solid state in the neighbourhood of the Rayleigh line. In the case of p-dichlorobenzene, however, not only some of these new lines but also some Raman lines due to intermolecular vibration of the single molecule are shifted on cooling the crystals once in ice, and it is not definitely known whether the lattice is changed with this cooling. On lowering the temperature of the crystals of the first two substances to that of liquid air, the new lines are shifted away from the Rayleigh line, but the linear coefficient of expansion calculated from the magnitude of these shifts with the help of the theory of lattice oscillation seems to be too high. The above results are discussed and it is suggested that the lines in question may have their origin in vibrations of polymerised groups.

INTRODUCTION.

It was shown by Bech and Ebbinghaus[1] that an abrupt contraction of volume takes place when crystals of p-dichlorobenzene, p-dibromobenzene, p-toluidine, sulphur and a few other organic substances are cooled below a certain critical temperature which is different for the different substances. From this observation they concluded that there are two modifications of the crystals of each of these substances. The modifications below and above the transformation point are called a- and β-modifications[2] respectively. Vuks[2] has recently studied the Raman spectra of the two modifications of crystals of p-dichlorobenzene and has observed that some of the new Raman lines which appear in the neighbourhood of the Rayleigh line in the spectrum of light scattered by the substance in the solid state, are shifted slightly with the transformation from one modification to the other. From this fact he has concluded that these lines have their origin

in lattice oscillatious. The arguments on which he has based his conclusion, however, do not seem to be very convincing. Therefore in order to investigate the question more thoroughly, the Raman spectra of crystals of p-dichlorobenzene, p-dibromobenzene and sulphur have been studied in the case of both the modifications and at different temperatures including that of liquid air. These results have been discussed in the present paper.

EXPERIMENTAL.

Kahlbaum's p-dichlorobenzene was distilled in vacuum in an apparatus made of pyrex glass. The distillate was collected in a wide tube forming a part of the above apparatus and solidified on cooling down to the room temperature. It was observed that whenever the solid mass was allowed to cool down to the room temperature, which was about 32°C, there was always an abnormal contraction of volume so that a conical hole with its axis along the axis of the tube was formed in the solid mass. The solid mass was melted again by immersing it in water bath at about 56°C, the melting point being 53°C, and was subsequently kept immersed in a water-bath at 45°C. The liquid this time solidified into a mass in which the axial hole mentioned above was absent. It appeared, therefore, that the solid mass obtained at 45°C was the β-modification and that at the room temperature was the α-modification, because according to Bech and Ebbinghaus the transformation point for this substance is 39.5°C. The Raman spectra of these apparent α- and β-modifications were photographed, keeping the crystals in the latter case always immersed in the water bath at 45°C and never allowing to cool down below this temperature after the substance had been melted and allowed to solidify. On examining the two spectrograms, the positions of the new lines appearing in the neighbourhood of the Rayleigh line were found to be identical in the two cases. The crystals were next cooled once in ice cold water and the Raman spectrum was again photographed. This time some of the new lines were observed to be shifted from their respective positions observed prior to the cooling of the crystals below the room temperature.

In the case of p-dibromobenzene, the crystals (Kahlbaum's) were melted in vacuum in a sealed pyrex tube and allowed to solidify and cool down to the room temperature. The transformation point in this case being 8°C, the β-modification was obtained at the room temperature. The Raman spectrum of this solid mass was photographed in the usual way, and that of α-modification was photographed by keeping the solid immersed in liquid ammonia contained in a transparent Dewar vessel.

In the case of sulphur a rhombic crystal was mounted on a small table and placed in an electric heater provided with suitable windows. The temperature of the crystal was gradually raised to about 85°C and keeping it constant, the

Raman spectrum was photographed. Next, the temperature was gradually raised to about 105°C and maintained constant and the Raman spectrum was again photographed.

The Raman spectra of the three substances mentioned above were photographed at the temperature of liquid air by keeping the substances immersed in liquid air contained in a transparent Dewar vessel. The Raman spectrum of p-di-dichlorobenzene in the liquid state was also recorded by keeping the substance immersed in a bath at about 60°C, in order to compare the spectrogram with that of the solid. Iron arc spectrum was photographed on each plate as comparison for measurement of wave-lengths. The dispersion of the spectrograph used was about 11.0Å/mm in the region of 4000Å.

RESULTS.

The values of $\Delta\nu$ of the new Raman lines observed in the case of p-dichloro-benzene and p-dibromobenzene under different conditions are given in table I along with those for the Raman lines due to sulphur. The estimated relative intensities of the lines are given in parentheses.

TABLE I.

Substance.	Tempera-ture.	Condition of experiment.	$\Delta\nu$ in cm^{-1} of the lines.	other changes observed.
p-Dichlorobenzene	45°C	melted and gradually cooled to 45°C.	40(2), 50(2) 82(2bd)	
	32°C	melted and gradually cooled to 32°C.	40(2), 50(2) 82(2d)	The lines 305 and 331 shifted to 308·6 and 327·5 respectively.
	32°C	the above mass once cooled in ice	46(2), 50(2) 92(2d)	
p-Dichlorobenzene	−180°C	the solid kept immersed in liquid air.	55 (2) 60 (2) 105 (2 s)	
p-Dibromobenzene	32°C	melted, solidified and cooled to 32°C.	36·0 (3) 93 (2 d)	
	−40°C	the solid kept immersed in liquid ammonia.	37·5 (3) 95 (2 d)	
	−180°C	the solid kept immersed in liquid air.	42 (3) 104 (2 s)	
Sulphur (incomplete)	32°C	rhombic crystal at 32°C	86 (2b) 154 (3) 220 (3) 467 (1·5)	
	85°C	crystal placed in a heater.	86 (2d) 158 (3) 220 (3) 467 (1·5)	
	105°C	„ „	„ „ „ 467 (2)	
	−180°C	crystal immersed in liquid air.	84 (2b) 158 (3) 220 (3) 467 (2)	

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DISCUSSION OF RESULTS.

It can be seen from the results given in table I that an abrupt change takes place in the positions of the lines 40 cm^{-1} and 82 cm^{-1} of p-dichlorobenzene on cooling the crystals once in ice and no such appreciable change takes place in the case of p-dibromobenzene even though the crystals are cooled in liquid ammonia. Since according to Bech and Ebbinghaus the transformation point is 39°·5 C, it might be expected that at 45°C, β-modification was obtained and at the room temperature they were transformed into the α-modification, and therefore, some difference ought to have been observed between the Raman spectra at the two temperatures. But such difference is not actually observed, and only when the crystals are cooled in ice-cold water and brought to the room temperature again, that some of the lines are shifted. Vuks, however, observed that sometimes the transformation from β- to α-modification does not take place unless the crystals are cooled below 22°C and the transformation from α- to β-modification takes place just above 37°C. Hence it might be assumed that in the case of the crystals studied by the present authors the β-modification persisted before they were cooled down below 22°C. But there seems to be a little difficulty in such an assumption. Bech and Ebbinghaus have observed that there is always a sudden abnormal contraction in volume accompanying the $\beta \longrightarrow \alpha$ transformation and it has been observed by the present authors that as a result of this contraction, a conical axial hole is produced in the solid mass even at the room temperature and no further abnormal contraction takes place on cooling the crystals in ice-cold water. Whether the crystals were transformed into the α-modification before being cooled below 22°C can be decided only by X-ray analysis of the crystals under the conditions mentioned above. But the data for these two conditions are not available. On examining, however, the results observed with p-dichlorobenzene with those for p-dibromobenzene, it is difficult to understand how the origin of the lines which are shifted in the former case with the transformation from β- to α-modification can be attributed to lattice oscillations. The transformation point in the case of p-dibromobenzene is 8°C and therefore, on cooling down to -40°C, certainly the α-modification was obtained. Hence if the new lines were due to lattice oscillations they ought to have been shifted also in this case in the same way as in the case of p-dichlorobenzene with the transformation from one modification to the other, because the two substances are isomorphic, but as can be seen from table I no such abrupt changes are observed.

Again in the case of p-dichlorobenzene, on cooling the crystals in ice-cold water and bringing them again to the room temperature, not only some of the new lines but also some of the lines due to intramolecular vibrations in the single molecule are shifted. The lines 305 cm^{-1} and 331 cm^{-1} observed at the room temperature before cooling are shifted respectively to 308·6 cm^{-1} and 327·5 cm^{-1} after the crystals are once cooled in ice and the Raman spectrum is

studied again at the room temperature. Also, the relative intensities of these two lines are widely different from each other in the former case but they are not so in the latter case. Hence there is some change in the relative intensities accompanying the shift in their positions. Since these lines are observed respectively at 297 cm⁻¹ and 329 cm⁻¹ in the case of the liquid state and are due to intramolecular vibrations in which the chlorine atoms are involved, it is evident that the intermolecular forces have influence on the positions of these lines and they are different in the case of the solid state from that in the case of the liquid, and also in the former case they are again not the same before and after the crystals are once cooled in ice. The shift of the lines 40 cm⁻¹ and 82 cm⁻¹ may also be due to the same reason and in this case also the chlorine atoms may be involved in the oscillations which take place in polymerised groups consisting of more than one molecule. Such a shift in the corresponding lines of *p*-dibromobenzene does not occur probably because the bromine atom being much heavier than chlorine atom, the frequencies are not affected appreciably by the intermolecular forces.

According to Vuks the new lines which are observed in the case of *p*-dibromobenzene at the room temperature are evidently those for the β-modification and they correspond to the lines due to *p*-dichlorobenzene in the following way :—

TABLE II.

p-Dichlorobenzene	(α-mod.)	Δν in cm⁻¹	27·5	46·5	54	93
,,	(β-mod.)	,,	43·3		54·5	82
p-Dibromobenzene	,,	,,	20·1		37·8	93

From the above arrangement it appears as if in the case of *p*-dichlorobenzene the line 27·5 cm⁻¹ for the α-modification is shifted to 43·3 cm⁻¹ with the transformation to the β-modification. It has been observed by the present authors however, that the line 27·5 cm⁻¹ is either not present at all, or it has not got any intensity comparable with that of the line 40·0 cm⁻¹ for the β-modification and it is the line 40 cm⁻¹ (given as 43·3 cm⁻¹ by Vuks) which is shifted to about 45 cm⁻¹ with the transformation. The presence of the line 20·1 cm⁻¹ in the case of *p*-dibromobenzene could not be verified by the present authors owing to the spreading of the Rayleigh line up to about 21 cm⁻¹ from the centre due to the presence of stray light which could not be avoided. The correctness of the assignment given in table II can, however, be tested by calculating the frequencies expected from any theory of lattice oscillation. Taking, for instance, the expression for the frequency of oscillation of a diatomic lattice given by Einstein [3]

$$\nu = C \times 0.77 \times 10^{12} \sqrt{\frac{T_s}{M v^{\frac{2}{3}}}}$$

where T, is the melting point, M is the molecular weight and v the molecular volume $= Nd^3$, N being the Avogadro's number and d the distance between the two atoms. Information regarding the magnitude of d can be obtained from results of X-ray analysis of the crystals. The crystal structure of p-dichlorobenzene and p-dibromobenzene has been analysed by Hendricks[4] who has reported the following dimensions of the cells.

	a	b	c	d_{100}	β	No. of mol.
p-Dichlorobenzene	14·83	4·1	5·88	5·88	112·30	2
p-Dibromobenzene	15·46	4·11	5·80	5·80	112·38	2

It will be observed that the primitive translations along a-axis in the two cases are slightly different from each other. The temperature at which the crystals have been investigated is not known. The crystals of the two substances have the same modification only if the temperature is either below 8°C or if it has never come below 22°C. As the investigation was carried out at Washington, the room temperature might have gone down during night below 22° C at the time of the investigation and consequently the crystals of p-dichlorobenzene might have been transformed from β- to α-modification and in that case the latter persisted even when the temperature rose above 22°C as has been explained previously. According to the above assumption there is some possibility that the crystals of p-dichlorobenzene and p-dibromobenzene studied by Hendricks had the α- and β-modifications respectively. If that be the case, it is evident from the dimensions of the unit cell given by him that there is very little difference between the two cases and the small difference in a may be due to the replacement of bromine by the chlorine atom. Hence, if the above assumptions be true, the shift of the Raman lines observed with the β⟶α transformation cannot be correlated with change in the frequency of lattice oscillations, because the lattice does not change appreciably with the transformation.

If, however, it is assumed that the two substances investigated by Hendricks were of the same modification, it can be seen that the value of d is almost the same in the two cases and if v and v' be the frequencies of oscillation of the lattices of dichloro- and dibromobenzene respectively, we have

$$\frac{v}{v'} = \sqrt{\frac{T.M'}{T.M}} = \sqrt{\frac{326 \times 236}{362 \times 107}} = 1\cdot41 \text{ approximately.}$$

The values of v/v' obtained from the assignment given in table II are shown in table III.

TABLE III.

ν in *p*-dichlorobenzene in cm.$^{-1}$		ν in *p*-dibromobenzene in cm.$^{-1}$		ν/ν' observed.	ν/ν' calc.
Vuks	Authors	Vuks	Authors		
20·1	—	43·3	40	2·0	1·41
37·8	36·0	54·5	50	1·39	,,
93	93	82	82	0·88	,,

It can be seen from the above table that except in the case of the line 50 cm^{-1} of *p*-dichlorobenzene, there is no agreement between the observed and calculated values of ν/ν'. Since the line 50 cm^{-1} is not shifted at all with the transformation, this agreement has no significance at all.

The results given in table I further show that the new lines due to the α-modification of both the substances are shifted away from the Rayleigh line when the crystals are cooled in liquid air. The linear coefficient of expansion of the substances can be calculated from the magnitude of the shifts of these lines as has been done previously by one of the present authors in the case of naphthalene. The accurate values of $\Delta\nu$ in cm^{-1} observed by the present authors in both the cases at the room temperature and at $-180°$C are given in table IV along with the values of α. the linear coefficient of expansion calculated from these values of $\Delta\nu$. The letters *d* and *s* in parentheses denote diffuse and sharp respectively.

TABLE IV.

p-Dichlorobenzene.				*p*-Dibromobenzene.		
	ν_1	ν_2	ν_3		ν_1	ν_2
32°C	40	50	92 (*d*)	$-40°$C	37·5	96 (*d*)
$-180°$C	55	60	105 (*s*)	$-180°$C	42	104 (*s*)
α calc. →	·00092	·00094	·00066		·00085	·00059

The above values of α are not very consistent with each other and when compared to the value ·00011 for naphthalene which has almost the same melting point as *p*-dibromobenzene, the values deduced in the present case seem to be too high. Further, there is a significant change in the properties of the line 92 cm^{-1} in both the cases with the lowering of temperature to that of liquid air. This line is very broad and diffuse at the room temperature and becomes very sharp at the low temperature in both the cases. In the case of *p*-dichlorobenzene

it has been observed that the line becomes broader at about 45°C than at the room temperature. Also, this line has the same position in the two cases at the low temperature.

In the case of sulphur, no change has been observed to take place in the position of the lines with the transformation from the rhombic to the monoclinic variety. This is consistent with the fact that the lines observed in this case are due to oscillations of the S_{16} and S_8 molecules and therefore their positions do not depend on the nature of the lattice. There is slight influence of the lattice, however, on the relative intensities of the lines, because the line 467 seems to be weakened with the transformation from rhombic to the monoclinic variety, as can be seen from the results given in table I. The intensity of this line also increases with the lowering of the temperature to that of liquid air and this change in intensity cannot be explained by Placzek's theory according to which the intensity should have diminished with the lowering of temperature.

Also, the line 86 cm^{-1} is shifted to 84 cm^{-1} at the temperature of liquid air.

From the above results it is suggested that the new lines in question may be produced by oscillations in polymerised groups as has been suggested previously by one of the present authors in other cases. The results of X-ray investigation of the two modifications of p-dichlorobenzene will be reported by the present authors shortly.

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PALIT LABORATORY OF PHYSICS,
92, UPPER CIRCULAR ROAD, CALCUTTA.

Note added in Proof. After this paper was communicated, a paper by Venkateswaran dealing with the Raman spectra of sulphur and phosphorus has appeared (Proc. Ind. Acad. Sci., A, 4, *p*. 414, 1936). He has observed a line at 36 cm^{-1} in the case of solid phosphorus and has also observed that the line 88 cm^{-1} of rhombic sulphur is shifted to 80 cm^{-1} in the case of monoclinic sulphur at 110°C. We have, however, observed that this line of sulphur remains exactly in the same position even when the rhombic crystal of sulphur is gradually heated to 105°C and kept at this temperature and it has been shown by Bech and Ebbinghaus that the monoclinic variety is obtained in this way at 105°C. Venkateswaran has calculated the frequency of the oscillation of the cubic lattice of phosphorus with the help of Lindemann's formula and the frequency 27·3 cm^{-1} so obtained has been identified with the frequency 37 cm^{-1} observed by him. He has also identified the frequency 88 cm^{-1} observed in the case of sulphur with frequency 100 cm^{-1} of the oscillation of the rhombic lattice of sulphur obtained from similar calculations. The actual discrepancy between these calculated and observed frequencies is about 25% in the case of the cubic lattice of phosphorus and it is only about 12% in the case of rhombic lattice of sulphur. Venkateswaran, however, thinks that the discrepancy in

the latter case is much larger than that in the former case and that this larger discrepancy in the case of sulphur is due to the fact that Lindemann's formula cannot be applied to the case of lattices other than cubic. He has also remarked, that for this reason the results obtained by one of us previously by applying such a formula in the case of monoclinic crystals of naphthalene are without any significance. This remark requires justification in view of the facts mentioned above and of the fact that by applying the same formula to the case of rhombic lattice of sulphur, Venkateswaran himself has drawn the conclusion that the line 88 cm⁻¹ of sulphur is due to lattice oscillation. On carefully examining the spectrograms it has been observed by us, however, that this line of sulphur is shifted at the temperature of liquid air by about 2 cm⁻¹ towards the Rayleigh line, *i.e.*, in a direction opposite to that expected from the theory of lattice oscillation. If, as Venkateswaran thinks, Lindemann's formula can be applied at least approximately to the case of sulphur, and the line 88 cm⁻¹ is assumed to be due lattice oscillation, it is difficult to understand the above change in position of the line with the change of temperature. It will be seen from the above facts that the conclusions drawn by Venkateswaran in the case of sulphur lack in foundation.

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