

LOW FREQUENCY RAMAN LINES IN ORGANIC CRYSTALS.

By C. S. VENKATESWARAN.

IMMEDIATELY following the discovery of the Raman Effect by Prof. Sir C. V. Raman in 1928, Krishnan in a Note to *Nature* (1928) reported six frequencies for crystalline quartz, out of which three namely, those at 127, 207 and 267 cm.^{-1} , were attributed by him (1929) as characteristic of the crystal as a whole and distinct from the inner vibrations of the molecules in the crystal. He also observed (1929) similar low frequency Raman lines for calcite and gypsum. Later Krishnamurti (1930) showed that a sharp and intense line with frequency varying from 230 to 155 appears in the crystals of certain inorganic nitrates, but vanishes when they are examined in aqueous solutions. He has suggested therefrom that this frequency in the nitrates owes its origin to the mutual vibrations of the metal ions and the NO_3^- ions in the crystal lattice and its magnitude depends upon the mass of the cation. The influence of increase of temperature on the position and character of the low frequency Raman lines studied by Brickwedde and Peters (1929) and Ornstein and Went (1935) also confirm the view that they are characteristic of the crystal lattice. In his investigations on the Raman spectra of calcite and aragonite Bhagavantam (1931) has further shown that the magnitude of these frequency shifts for the same chemical individual depends on its crystal structure.

Similar low frequency Raman lines in organic crystals with shifts ranging from 20 to 130 cm.^{-1} were for the first time observed by Gross and Vuks (1935) in benzene, diphenyl ether, dibromobenzene and naphthalene. The fact that these lines in organic solids fall in the region where the 'wing' in the liquid appears, has led these authors (1936) to postulate that the latter is almost completely made up of these lattice Raman lines which become diffuse and merge with one another in the liquid state. These conclusions of Gross and Vuks regarding the origin of these lines in the crystals and their relation to the 'wing' in the corresponding liquids have been questioned by Sirkar. In a series of communications dealing with this subject, Sirkar and Gupta (1936-38) have put forward the suggestion that these low frequency lines owe their origin to intermolecular oscillations of polymerised groups of molecules in the solids, which are bound together by a weak electronic bond. The present investigation with organic crystals was

undertaken with a view to throw some light on the origin of these lines in crystals and their bearing on the 'wing' in liquids.

Experimental.

The substances examined were Kahlbaum's pure chemicals further purified by slow distillation in vacuum into the experimental tube. The molten liquid is cooled slowly till it sets into a translucent mass below the melting point. Though the solid thus obtained is polycrystalline, parasitic light is very much reduced in the scattered spectrum and reasonably good pictures are obtained with clear lines in the neighbourhood of the Rayleigh line. For an investigation of this character the choice of a proper spectrograph is of the utmost importance. Most of the spectrographs generally used for photographing Raman spectra possess a well-defined coma consisting of one or more broad bands on the Stokes side, round about 100 cm.^{-1} from the Rayleigh line. This instrumental defect is shown markedly by several of even the high grade spectrographs installed in this laboratory. This coma is comparatively very feeble in the Hilger two-prism glass spectrograph and is noticeable only in very heavily exposed spectrum plates. The latter instrument was, therefore, used in the present investigation and care has been taken to eliminate errors arising from this defect. Though the dispersion of this spectrograph is only 22 \AA. per mm. in the 4046 \AA. region, due to the large size of the prisms and lenses its resolving power is considerably greater than that of either the Fuess spectrograph having a dispersion of 18 \AA. per mm. used by Sirkar or the one employed by Gross and Vuks in their investigations. This has enabled the author to obtain correct estimates of the width of these lines at various temperatures. The temperature of the crystals is varied by means of an electric heater surrounding the whole of the experimental tube. The plates are measured with the aid of a Hilger cross-slide micrometer and the accuracy in the case of sharp lines is of the order of 1 cm.^{-1} .

Results.

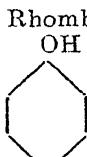
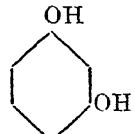
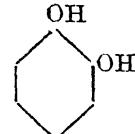
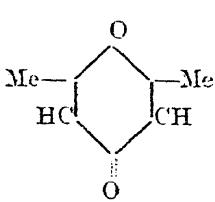
The results of the investigation are given in Table I* and some photographs of the spectra are reproduced in the accompanying plates. Table II gives the data on the low frequency Raman lines in organic crystals so far published by other authors.

The following observations may be made on the results obtained in the present investigation. All compounds containing the benzene nucleus yield in general four lines with frequency shifts ranging from 20 to 130 cm.^{-1}

* Note: The complete spectra of coumarin and dimethyl- γ -pyrone as well as some of the other compounds will be reported in a separate communication.

TABLE I.

Exciting Line $\lambda = 4046 \text{ \AA}$. For No. 12 exciting line is 4358 \AA .

No.	Substance	Crystal and Molecular Structures	Temperature in $^{\circ}\text{C}$.	Raman Frequencies in cm.^{-1}			
				38 (3)	72 (5 b)	93 (2 b)	116 (4 b)
1	Phenol M.P. 41° C.	Rhombic 	25°	38 (3)	72 (5 b)	93 (2 b)	116 (4 b)
			38°	One band with sharp edge ending at 110			
2	Benzoic acid M.P. 122° C.	Monoclinic $\text{C}_6\text{H}_5\text{-COOH}$	25°	38 (2)	62 (4)	101 (6)	126 (1 b)
3	Salicylic acid M.P. 159° C.	Monoclinic $\text{OH-C}_6\text{H}_4\text{-COOH}$	25°	43 (2)	64 (5)	95 (2)*	117 (1 b)*
4	Resorcinol M.P. 110° C.	Rhombic 	25°		70 (5 s)	(Incomplete)	
5	Catechol M.P. 105° C.	Monoclinic 	26°	36 (4)	56 (5)	78 (2)	110 (1)
			52°	36 (5)	55 (6)	77 (2)	108 (1)
			86°	35 (4)	55 (7)	77 (1)	108 (0)
6	<i>p</i> -Dichloro-benzene M.P. 53° C.	Monoclinic $\text{C}_6\text{H}_4\text{Cl}_2$	25°		48 (6 b)		89 (6 b)
			45°		43 (6)	55 (5)	88 (5 b)
7	Phthalic acid M.P. 206° C.	Rhombic $\text{C}_6\text{H}_4(\text{COOH})_2$	25°			81 (3)	
8	Dimethyl γ -pyrone		25°		48 (2 b)		101 (2 b)

* These two lines appear as a single broad band on the Stokes side.

TABLE I (Contd.)

No.	Substance	Crystal and Molecular Structures	Temper-ature in °C.	Raman Frequencies			
9	Coumarin M.P. 71°	Rhombic	25°	39 (5)	55 (6) 69 (2)	96 (5)	112 (5)
			60°	38 (5)	55 (6) 69 (1)	94 (4)	109 (4)
			68°	38 (5)	55 (6) 68 (1)	93 (4)	109 (4)
			70°	38 (5)	54 (6) 67 (1)	103 (2 b)	
10	Naphthalene M.P. 80°	Monoclinic	25°	46 (5)	74 (10)	108 (4)	121 (2)
			65°	46 (4)	74 (10)	105 (4)	118 (2)
			75°	46 (3)	72 (10)	102 (3 b)	
11	Diphenyl M.P. 70° (C ₆ H ₅) ₂	Monoclinic	25°	49 (3 b)	75 (2 b)		150 (1 b)
12	Benzophenone (C ₆ H ₅) ₂ CO M.P. 48°	Rhombic	25°		67 (3)		102 (5 s) 122 (1)
13	Salol M.P. 43°	Rhombic HO·C ₆ H ₄ ·CO O·C ₆ H ₅	25° —180° (glass)		71 (1 ?)	96 (5 s)	No lines and no wing
14	Chloroacetic acid	Rhombic CH ₂ Cl·COOH	25°		54 (2 s)		

TABLE II.

No.	Substance	Chemical Formulae	Temper- ature in °C.	Raman Frequencies				Reference
1	Benzene	C_6H_6 (Rhombic prismatic)	— 0°	62 (4 b)			104 (2 b)	G. and V. *
	„	„	— 180°	81	98 (b)	125		S. and G.
2	Diphenyl ether	$(C_6H_5)_2O$ (Rhombic)		22 (6 s)	38 (2 s)	67 (8 b)	104 (10 b)	G. and V. * and S.
3	Naphthalene	$C_{10}H_8$	0°	45 (4 s)	73 (8 b)	109 (3)	124 (2)	„
	„	„	— 180°		80	120	140	S.
4	p-Dibromo- benzene	$C_6H_4 \cdot Br_2$ (Monoclinic)		20 (8)	38 (8)		93 (6 b)	G. and V. *
5	p-Dichloro- benzene	$C_6H_4 \cdot Cl_2$ (Monoclinic)	< 25°	27	46	54	93 (b)	V *
	„	„	> 33°		43	55	82 (b)	„
6	p-Bromochloro- benzene	$C_6H_4 \cdot Cl \cdot Br$ (Rhombic or monoclinic)		22	43		94 (b)	„
7	Chlorobenzene	C_6H_5Cl		49	67	86	105	S. and G.
8	Cyclohexane	C_6H_{12}			60		105	M.
9	Dichloro- ethylene	$CHCl : CHCl$			53 (st.)			S. and G.
10	Acetic acid	CH_3COOH			49 (v.st.)		119 (v.w.)	Sid.
11	Chloroform	$CHCl_3$			75		94	S. and G.
12	Bromoform	$CHBr_3$ (Hexagonal)			32-55			Sid.

G. and V. = Gross, E., and Vuks, M.; V. = Vuks, M.; S. = Sirkar, S. C.; S. and G. = Sirkar, S. C., and Gupta, J.; M. = Mitra, S. M.; Sid. = Sidorenko, A. I.

* The numbers within brackets are estimates of relative intensities obtained from the published photographs.

provided the lines are fairly sharp and the spectrum is intense. There is a general similarity in their low frequency spectra and in most cases the fourth frequency which has a shift of more than 100 cm.^{-1} is nearly double the second. The latter line which appears round about 60 cm.^{-1} is one of the most intense lines of this group and in all cases it has greater intensity than the one preceding. Apart from these similarities, the magnitude of the frequencies varies from compound to compound.

As illustrated in the accompanying plates, the width of the lines also varies considerably with the nature of the substance. In coumarin, catechol, benzoic acid and salicylic acid all the lines except the outermost one are fairly sharp; in paradichlorobenzene and naphthalene they are broad and in diphenyl they are very broad. The great breadth of some of these lines may be due to their composite character. Sirkar has shown that at liquid air temperatures these lines sharpen just as other molecular vibrations themselves do. But on raising the temperature up to the melting point no appreciable effect is observed on the first two lines. The outermost frequency, however, shows a measurable diminution due to the expansion of the crystal and diffuses out slightly as illustrated in Figs. 1 to 5. In passing over to the liquid state, there is a sudden transition, the lines being completely replaced by a wing whose intensity is great near the Rayleigh line. In phenol (Fig. 2), four broad lines of almost equal intensity appear just resolved at the room temperature, but at 38° C., that is, just below the melting point, due to further broadening of the lines, the structure of the pattern is lost and instead, a band sharply ending at 110 cm.⁻¹ appears on the plate. The author is unable to confirm the change in the spectra of *p*-dichlorobenzene at less than 25° C. and greater than 33° C. reported by Vuks (1937) and attributed to change of crystal form, even though the substance was kept for well over a week at ice-cold temperature before the spectrum at 25° C. was taken. The minor changes in the spectrum of this compound given in Table I are to be explained as caused by changes of temperature alone unaccompanied by change of crystal structure.

Liquid benzophenone in the supercooled state gives a well-defined band at 102 cm.⁻¹ corresponding to the sharp line in the solid in that position. The wing, however, is less prominent in the liquid. The persistence of this band in liquid benzophenone has also been previously observed by Gross and Vuks (1935). A similar observation has been made by the latter authors and by Sirkar (1936) for diphenyl ether. In diphenyl also, corresponding to the broad line at 150 in the solid, there is a band at 140 in the liquid (Mukerji, Aziz, 1938).

Distilled salol in vacuum remains in a transparent glassy state up to the liquid air temperatures. The glass softens to the liquid condition much below the melting point as the temperature is raised. The spectra of the light scattered by the glass at liquid air temperature and the liquid salol are given in Fig. 7. In the glass a continuous spectrum is present which masks the Raman lines beyond 400 cm.⁻¹ to some extent. In spite of this fact, for the same intensity of the spectra of the glass and the liquid as judged from the intensity of the Raman lines of larger frequency shifts, the

glass shows neither a wing nor any line near the Rayleigh line, whereas the liquid gives a fairly intense wing characteristic of the liquid state. The crystals of salol prepared by the method described earlier form an opaque mass and yield Raman lines only on long exposures. Though under these conditions the region near 4046 Å is affected by halation, one fairly intense and sharp line at 96 and one faint line at 70 could be identified on the plates.

Discussion.

Origin of low frequency Raman lines.—The influence of temperature on these lines in the crystals and especially their total disappearance as discrete lines in liquids are characteristic features which suggest that they are not due to intramolecular vibrations but are intermolecular in origin. Gross and Vuks (1935) have attributed these lines to oscillations of the crystal lattice. Sirkar (1936) avers that the change in the polarisability involved in a lattice oscillation is too small to account for the great intensity of these lines as compared to the intense Raman lines of the molecule. He has also pointed out other considerations such as the persistence of these lines in some liquids and solutions, the differential changes in frequencies of various lines of one and the same crystal due to changes of temperature and the inadequacy of these lines to account for the heat content of these crystals by their Debye functions, as obstacles in the way of assigning them to crystal oscillations. Based mainly on his arguments against their lattice origin, he has suggested that they arise from intermolecular oscillations of polymerised groups in the solid.

The following considerations are, however, in favour of attributing these lines to lattice oscillations in the crystal. (1) The results given in Tables I and II show that in the case of benzene derivatives, though there are certain general similarities in the spectra, considerable variations occur in the magnitude, intensity and breadth of the respective lines due to changes both in the molecular structure and in crystal form. The change due to crystal structure alone is particularly noticeable in resorcinol and catechol having very similar chemical formulæ, the intense line at 70 cm.⁻¹ in the former appearing at 55 cm.⁻¹ in the latter. Benzoic acid and salicylic acid having similar crystal structures, on the other hand, show a small difference only in the intensities of the lines, which is due to the difference in their molecular formulæ. (2) In inorganic crystals of the ionic type the lattice Raman lines are known to fall in the region between 100 to 300 cm.⁻¹ When the force between the oscillating mass points is valence as in diamond the frequency is very much higher. In the organic crystals belonging to the molecular type of lattices, the intermolecular forces are weaker than the electrostatic forces in ionic crystals and consequently the lattice frequencies

should be correspondingly lower. The experimentally observed Raman lines are of the expected magnitude. (3) It has been observed in a large number of organic crystals (Figs. 1 to 5) that as the temperature is raised these lines retain almost the same breadth up to the melting point. In the case of ionic crystals, as far as it is known, these lines become more diffuse at higher temperatures. This is well illustrated by the beautiful photographs of the spectra of sodium nitrate taken at different temperatures by Nedungadi (1938). This difference in the behaviour of ionic and molecular crystals may be explained as follows: If A and B are two points connected together by a force f , the frequency of oscillation ν is given by $\nu = 2\pi \sqrt{f/m}$, where m is the reduced mass. In the case of ionic lattices the distance between the oscillating units is small and the force is great. During an oscillation, these two units, A and B approach and recede from each other and the force f varies between a maximum and a minimum. It is thus easy to see that ν will cease to be monochromatic and give rise to a broad Raman line. With the rise of temperature, this variation of force and consequently the breadth of the line will also increase. In the case of molecular lattices the distance between the mass points is generally larger and the force is less than for the ionic and the variation in the force during mutual oscillations of the units is relatively small; changes due to rise of temperature is negligible, provided the amplitude of the oscillations remains small, as is the case so long as the solid state is maintained. This accounts for the fact that no appreciable change is observed in the sharpness of the lattice lines in organic crystals in which only residual molecular forces are responsible for such oscillations. No proper explanation is possible for this difference in the behaviour of molecular and ionic crystals on the theory of polymerisations postulated by Sirkar. (4) It is significant to note that while salol crystals have yielded one sharp and fairly intense line at 96, no such line is observed in the glassy state. There is more likelihood of polymers existing in glasses than in crystals. The fact that the line is not recorded in the glass indicates that a crystalline lattice in which units are oscillating with definite phase relationship with each other is necessary to produce these low frequency lines.

Oscillations of molecules which constitute the mass-points of a crystal lattice can be produced by a displacement from an equilibrium position resulting from the intermolecular forces, either by a translation or by a rotation through small angles about the centre of gravity. The frequency of a translational oscillation is determined by the intermolecular forces and the masses of the oscillating units and that of a rotational oscillation depends on the moment of inertia of the molecule. As has been pointed out by Sirkar,

the mutual oscillations of either type of a single pair of molecules or groups of molecules may not produce sufficient change in polarisability to yield an intense Raman line in light scattering. But the crystal is an elastic continuum and the several units in the lattice oscillate with a definite phase relationship with each other. It may be assumed that at any instant during an oscillation when a molecule approaches the neighbouring molecule on one side, its opposite neighbour will be receding from it so as to maintain the centre of gravity. The cumulative effect of this is to render the change in polarisability in a finite volume sufficiently large to account for the appearance of intense Raman lines. The results of the present investigation indicate that the outermost lines at about 100 cm.^{-1} are to some extent broad and diminish in frequency and diffuse out as temperature is increased up to the melting point. The lines nearer the Rayleigh, on the other hand, retain their sharpness and show proportionately small changes in frequency at these temperatures. The difference in the behaviour of these lines suggests that the outermost line is due to translational oscillations of the lattice and the intense lines of smaller frequencies are due to the flexural oscillations of the lattice involving 'hindered rotation' of molecules. The anomaly pointed out by Sirkar in the changes of these frequencies at different temperatures and in crystals of similar molecular structure is thus due to a difference in the nature of oscillations responsible for each of these lines. In a note to *Current Science*, the author (1937) pointed out that in the cubic crystals of CO_2 , the sharp line at 58 cm.^{-1} agrees with the lattice frequency calculated from the Lindemann's formula and is of the same order of magnitude as the frequency of hindered rotation of the molecules calculated on the lines indicated by Pauling (1930) for linear molecules. This agreement has led to the suggestion that this line is due to a flexural oscillation of the lattice of the type indicated above. In a recent paper Sirkar and Gupta (1938) have criticised this view of the author on the basis that the heat content of solid CO_2 calculated from the Debye function of this frequency does not agree with the observed facts. Similar considerations have been advanced by them to rule out the lattice origin for the lines in sulphur and benzene. It may be pointed out that Debye functions are applicable only to *continuus* radiations having frequencies ranging from zero to a limiting value ν_m , the existence of which is demonstrated by the fine structure of the light scattered by solids (Raman and Venkateswaran, 1938). The lattice vibrations have a definite frequency and yield a *discrete* line just as the molecular vibrations do. Hence for the calculation of the specific heat of a solid, the Einstein functions of these frequencies are more appropriately applicable than the Debye functions. If calculations of specific heat are made on this basis, taking into account

the degeneracies involved in a particular oscillation, the discrepancy discovered by Sirkar and Gupta disappears.

In relation to the wing in liquids.—Gross and Vuks (1936) have postulated that the lattice Raman lines in solids broaden and give rise to the wing that is observed on either side of the Rayleigh line in liquids. The chief characteristics of this wing in liquids are its great intensity at or near the Rayleigh line and its rapid but continuous fall upto a limit which varies from liquid to liquid. It is prominent only in anisotropic molecules and is depolarised to an extent of 6/7 throughout its entire region. Rao (1934) and Gross and Vuks (1935) have reported that there is no observable difference in the distribution of the intensity or its extension with the rise of temperature upto the boiling point, except in the region from 0 to 20 cm.⁻¹ where according to the latter authors there is an increase in intensity with rise of temperature for certain viscous liquids. Though on a rough estimate the wing in the liquids and the lines in the solids show some correspondence (Sidorova, 1937), careful examination of Figs. 1, 2 and 3 will reveal important differences in the extent and distribution of intensity in either case. Thus in coumarin and naphthalene the lines exist up to 110 to 120 cm.⁻¹ whereas the wing, in equally exposed plates, extends only up to about 70 or 80 cm.⁻¹ In phenol, the extension of the wing is greater than for the lines. Secondly, the line at about 50–60 cm.⁻¹ is the most intense in the lattice spectra, but the wing shows no maximum at this point. Thirdly, if the major portion of the wing in liquids is vibrational in origin, it has to be postulated that a quasi-crystalline structure exists in the liquids and remains the same upto the boiling point, in order to interpret the results obtained with the wing at higher temperatures satisfactorily. This is highly improbable. Fourthly, glass itself being a supercooled liquid, the discrete lines in the crystals should exhibit themselves either as a wing as in liquids or as broad bands. Author's results with salol, glass and liquid, conclusively show that this is contrary to facts (Fig. 7). Fifthly, Gross and Vuks (1935) themselves have observed that these lattice Raman lines in solids show a depolarisation factor varying from $\rho = 0$ to $\rho = 1$, and this does not fit in with the observations of all investigators that the wing in liquids is depolarised to an extent of 6/7 throughout its entire region. Sirkar and Gupta have also adduced other evidence to show that the wing and the low frequency Raman lines are not connected with each other. The obvious conclusion arising from these considerations is that the wing in liquids is an entirely independent manifestation of the properties of molecules in a state of rotation in a random fashion in the medium. The discrete lines arising from translational or flexural oscillations of the lattice cease to exist in the liquid, and the hindered

rotation of molecules involved in the flexural oscillations is replaced by complete rotation in the liquids, provided the viscosity is not very great. As suggested by Raman and Krishnan (1928), this molecular rotation gives rise to the wing in liquids, with a distribution of intensity similar to that observed by Bhagavantam and Rao (1934) and Weiler (1935) for gases above critical pressures.

There is one fact, however, which needs explanation. In liquids, benzophenone, diphenyl and diphenyl ether, a well-defined band appears in the place of the line above 100 cm.^{-1} in the solids and is observed to persist even at high temperatures and in dilute solutions. These three compounds possess two benzene rings linked through a valence bond. According to the present author, this band arises from deformational oscillations of these two rings against each other and thus appears to be intramolecular in origin and have nothing to do with either the lattice oscillations as suggested by Gross and Vuks or with polymerisation as postulated by Sirkar. A similar oscillation which gives rise to a depolarised Raman band below 200 cm.^{-1} has been observed by Saxena (1938) for bicyclic compounds.

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman for his continued interest and valuable suggestions in the course of the work.

Summary.

The Raman spectra of the low frequency region between 20 and 130 cm.^{-1} have been recorded for fourteen organic solids and the influence of rise of temperature upto the melting point on these lines in a few cases has been investigated. These lines in the solids are interpreted as arising partly from translational and partly from rotational oscillations of the molecules with definite phase-relationship with each other in the lattice. Liquid salol exhibits a fairly intense wing near the Rayleigh line which does not appear in salol glass at liquid air temperature. This observation and other experimental facts such as extension of the wing, the distribution of intensity and the influence of temperature on it and the degree of depolarisation at different points in the wing and the corresponding lines in the solid do not support the hypothesis of Gross and Vuks that most of the wing in liquids arises from the lattice Raman lines and that the liquid state is quasi-crystalline in structure. A band observed in liquids, benzophenone, diphenyl ether and diphenyl in the place of a line above 100 cm.^{-1} in the solids is attributed to a deformational oscillation in the molecule itself, which seems to be characteristic of bicyclic compounds.

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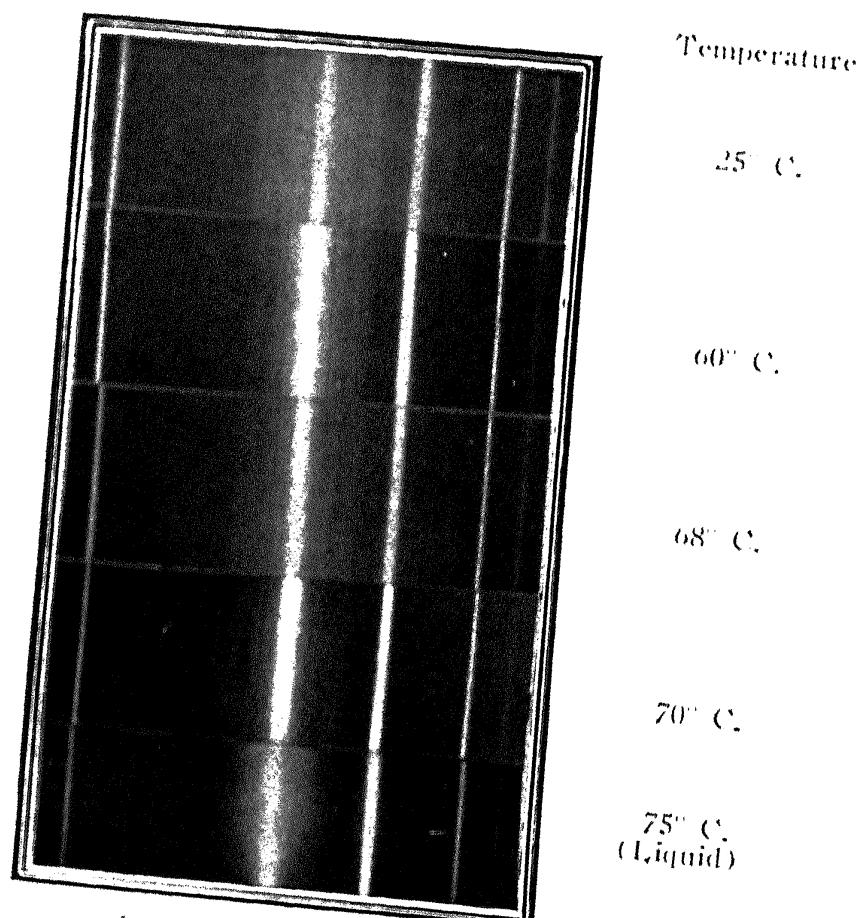


FIG. 1. Commarin.

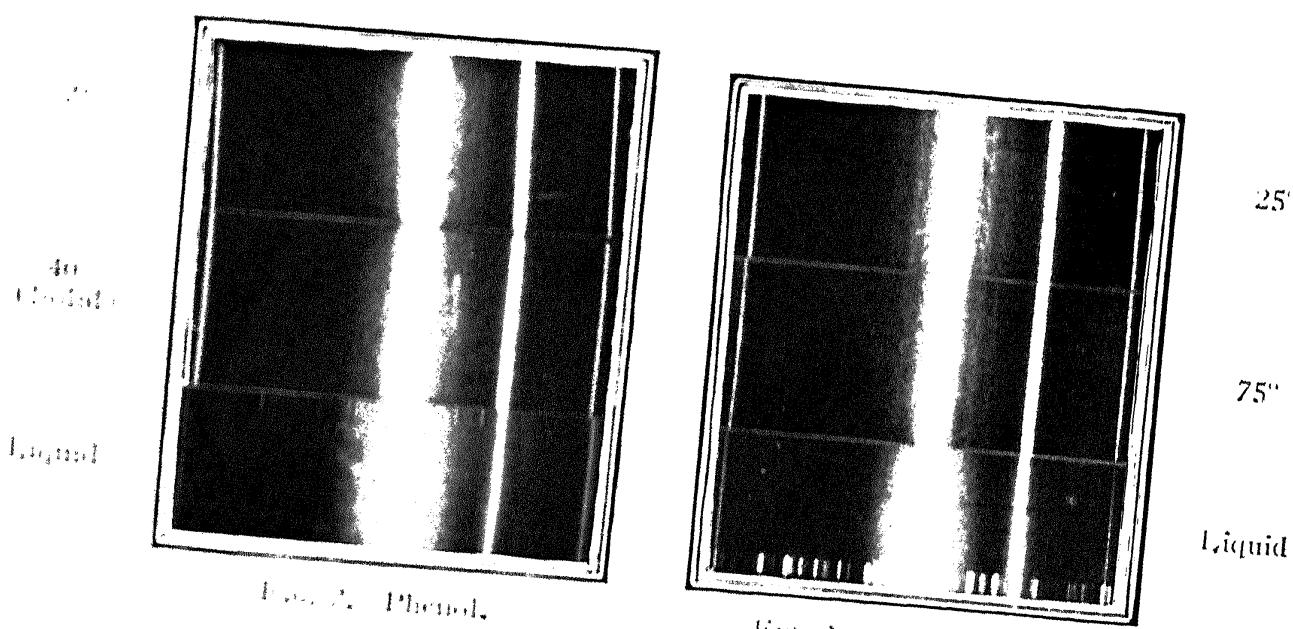


FIG. 2. Phenol.

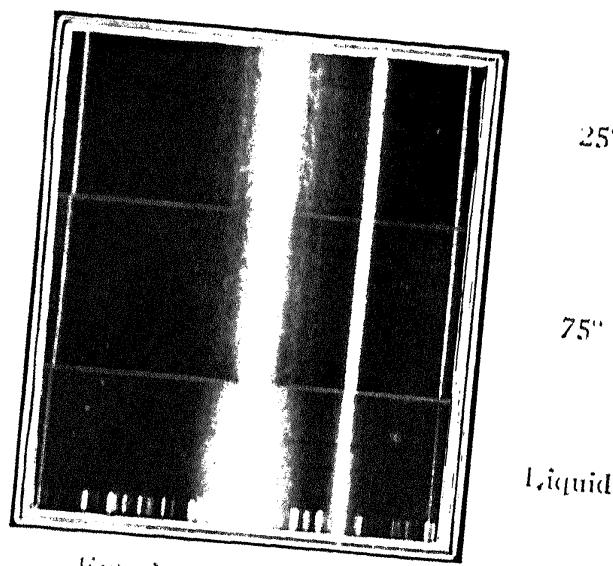


FIG. 3. Naphthalene.



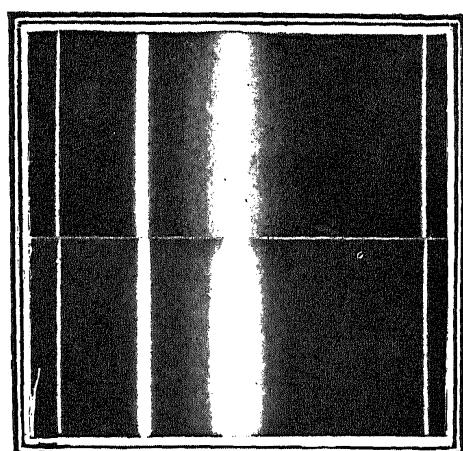


FIG. 4. Catechol.

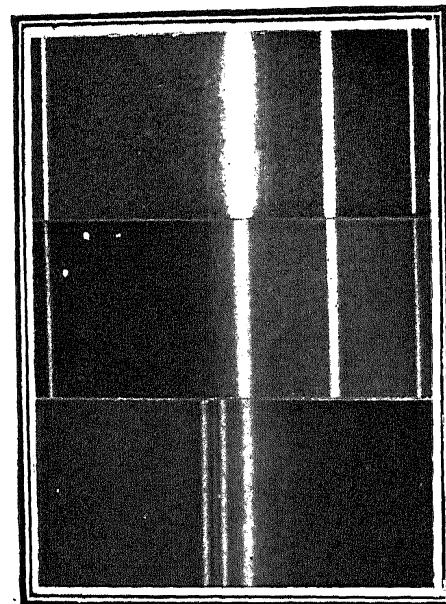


FIG. 6.

Benzoic
acid

Diphenyl

Do.

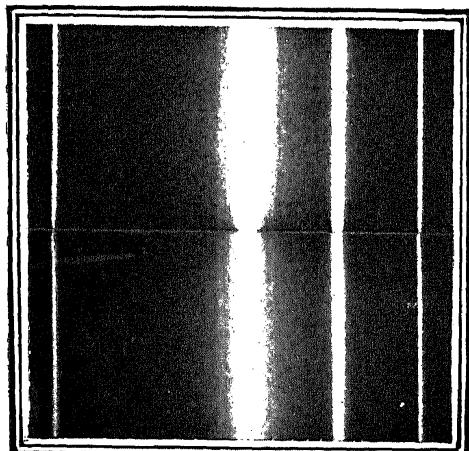


FIG. 5. Dichlorobenzene.

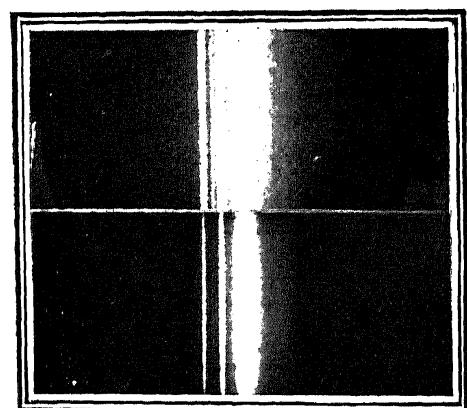


FIG. 7. Benzophenone.

Solid

Supercooled
Liquid

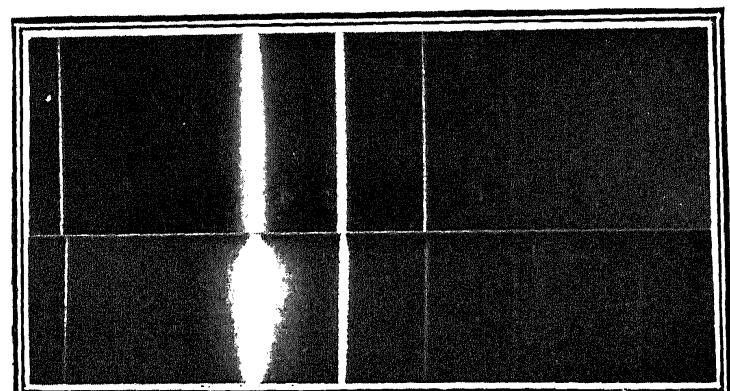


FIG. 7. Salol.



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