HINDERED ROTATION AND OSCILLATION OF MOLECULES IN LIQUIDS AND IN CRYSTALS.

By S. Bhagavantam.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

1. Introduction.

Extensive experimental investigations by Weiler,[1] Trumpy,[2] Rousset,[3] Ranganadham,[4] Bhagavantam[5] and Veerabhadra Rao[6] on the rotational Raman effect in liquids have brought to light certain characteristic features which are not in agreement with the predictions of the existing theories. This is probably connected with the fact that the latter are all based on the assumption of freely rotating molecules, a condition which is presumably not fulfilled in liquids or dense fluids. Nevertheless, liquids do exhibit wings on either side of the Rayleigh lines which are apparently connected with the optical anisotropy of the molecules. These must therefore be interpreted as Raman radiations arising in a manner which in some respects at least is analogous to the origin of rotational Raman scattering in gases. A satisfactory explanation of these phenomena is of fundamental importance from the point of view of the liquid state, and for this purpose, a new suggestion is made in the present paper which is based on some ideas put forward by the author in an earlier communication.[5] A brief review of the other explanations that have so far been offered is also presented.

2. Characteristics of Rotational Raman Scattering in Liquids.

In the communications referred to above, it has been shown that the intensity of the rotation wing in all the liquids studied, with the exception of liquid hydrogen, starts from being a maximum at or very near the centre of the Rayleigh line, falls off rapidly till a certain distance is reached and then only gradually fades away lingering on to such distances as are wholly irreconcilable with the view that the entire wing is due to single and normally rotating molecules. The existing theories, on the other hand, predict that the intensity should start from being zero near the centre, increase till a certain point is reached where the wing exhibits a maximum intensity and then fall off somewhat abruptly. Thus the experiments differ from the theoretical results in three important respects, *viz.*, (i) absence of a maximum of intensity at a specified point well separated from the centre, (ii) concentration of intensity in the neighbourhood of the centre, (iii) extension of the wing to large distances from the centre.

63

In two communications Gross and Vuks[7] have recently published results of great significance in this connection. They find that the continuous spectrum in the remoter regions of the wings exhibited by diphenyl ether, benzene and naphthalene in the liquid state is replaced by separate lines in the Raman spectra of these substances when studied in the solid state. In addition, the continuous spectrum close to the Rayleigh line altogether disappears in all these cases as we pass from the liquid to the solid state.

3. Explanation of the Results.

The author has attempted to account for the observed results in liquids in an earlier paper already referred to, by assuming that the molecules in a liquid are arranged in a quasi-crystalline manner, the crystalline arrangement being akin to that which is present in the corresponding solid state. Forces similar to those in the crystal will exhibit between the neighbouring molecules of the liquid and an extension of Pauling's[8] work on "The Rotation of Molecules in Crystals" at once tells us that the liquids can in general be divided into two classes : one set of liquids, examples of which are liquid hydrogen, nitrogen, oxygen, etc., in which most of the molecules are freely and normally rotating in spite of the quasi-crystalline arrangement, the other set of liquids, examples of which are molten iodine, benzene and others composed of heavy molecules, in which most of the molecules are executing only small oscillatory motions about their equilibrium positions which may be called incomplete rotations. The quasi-crystalline forces in these cases hinder free rotation and the oscillatory motion can pass over into a complete rotation only if the temperature is sufficiently high. It has been suggested that these oscillatory motions which are very imperfectly quantised in liquids are responsible for the extended regions of the so-called rotation wings, and the recent results of Gross and Vuks lend strong support to such a view. As soon as the substance is crystallised the oscillations become definitely quantised and appear as separate lines in the scattered light. Further evidence in support of this view which will be presented in this paper is as follows.

Pauling's theory permits us to make a rough computation of the frequencies that are to be expected.* Taking the specific case of benzene, it is seen that its specific heat reaches a value of 5 cal/grm. mol., at a temperature of $34 \cdot 5^\circ$ K. This would mean that $h\nu_0/k$ for benzene is $103 \cdot 5^\circ$ K where h and k have the usual significance and ν_0 represents the frequency of oscillation. From this ν_0 may be evaluated as 72 cms.$^{-1}$ Gross and Vuks have actually observed two lines at 63 cms.$^{-1}$ and 108 cms.$^{-1}$ The

---

* For details of computation, see L. Pauling, *Phys. Rev.*, 1930, **36**, 430.

order of magnitude is very satisfactory in view of the assumptions involved and the fact that the benzene crystal is not a cubic one may be responsible for the splitting up of the oscillation into two different frequencies.

Moreover, the idea of an incomplete rotation at once shows that just as in the case of normally rotating molecules, the optical anisotropy will play an important part in deciding the intensities of these lines. This conclusion is in accordance with the observed fact that such extended wings are usually exhibited prominently only by substances like benzene, naphthalene, carbon disulphide, etc., which are highly optically anisotropic.

It must be pointed out here that the explanation offered by Gross and Vuks that they are due to "vibrations characteristic of crystalline lattice" is essentially different from the foregoing views. In the opinion of the author, such lattice oscillations are different and examples of the same can be found in the Raman spectra of calcite, aragonite, etc. A serious defect of such an explanation is that one does not see any obvious relationship between the intensity of the corresponding Raman scattering and the optical anisotropy of the substance, whereas experimental results clearly show that only strongly anisotropic substances exhibit this phenomenon either as lines in solids or as continuous and extended wings in liquids.

4. Summary.

The extended portion of rotation wings in liquids and the separate lines which take their place in the corresponding solids are explained as due to small oscillatory motions of molecules about their equilibrium positions. The motion is properly quantised in solids on account of the perfect crystalline arrangement and results in distinctly separated lines possessing definite frequency shifts. In liquids, there is only an imperfect quantisation on account of the quasi-crystalline arrangement and this results in a broadening of the lines into a continuous wing. A rough computation of the oscillation frequency in benzene from the specific heat data on the lines indicated by Pauling gives 72 cms.$^{-1}$ which is of the expected order of magnitude. These oscillations, as pictured by Pauling, may be regarded as incomplete rotations and such a picture involves a direct relationship between the optical anisotropy of the molecule and the intensity of the scattered line. This is in accordance with the experimental fact that only substances like benzene and naphthalene which have a marked degree of anisotropy give rise to extended wings in the liquid state and lines in the solid state.

A5

F

S. Bhagavantam

REFERENCES.

1. I. Weiler, *Z. f. Phys.*, 1931, **68**, 782.
2. B. Trumpy, *D. Kgl. N.V.S.*, 1932, 5, Nos. 16, 18, 47.
3. A. Rousset, *J. Phys. et le Rad.*, 1932, **3**, 555.
4. S. P. Ranganadham, *Ind. Jour. Phys.*, 1932, **7**, 353.
5. S. Bhagavantam, *Ind. Jour. Phys.*, 1933, **8**, 197.
6. A. Veerabhadra Rao, *Proc. Ind. Acad. Sci.*, 1934, **1**, 274.
7. E. Gross and M. Vuks, *Nature*, 1935, **135**, 100 and 431.
8. L. Pauling, *Phys. Rev.*, 1930, **36**, 430.