

# THE RAMAN SPECTRA OF SULPHUR AND PHOSPHORUS.

## Part II. Lattice Oscillations.

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### 1. Introduction.

THE phenomenon of wings accompanying the Rayleigh line in light scattering in liquids has been the subject of detailed investigation by several authors<sup>1</sup> in recent years. If this wing is to be considered as purely due to rotation of molecules as in gases, the existing theories predict that its intensity should start from a minimum near the exciting line and increase to a maximum and then fall off gradually. Experimentally, however, it has been observed that the intensity is a maximum at the Rayleigh line and extends on either side far more than is to be expected purely due to rotation of molecules. This discrepancy has been explained by Bhagavantam<sup>2</sup> who has postulated that some highly anisotropic quasi-crystalline groups of molecules exist in liquids and the 'hindered rotation' of molecules in these groups gives rise to a continuous Raman band whose superposition on the genuine rotational scattering is responsible for the observed effects.

A direct experimental proof for the above postulate of Bhagavantam was furnished by the recent discovery of Gross and Vuks<sup>3</sup> who established by beautiful photographs that the continuous wing observed in benzene, diphenyl ether, *para*-dibromobenzene and naphthalene breaks up into discrete intense lines when these substances are examined in the state of single crystals. They have attributed these new lines to the characteristic oscillations of the crystal lattice. According to them the wing accompanying the

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<sup>1</sup> Weiler, *Z. f. Phys.*, 1931, **68**, 782; Rousset, J., *Jour. de Phys. et la Rad.*, 1932, **3**, 555; Trumpy, B., *Kgl. N.V.S.*, 1932, **5**, 16, 18 and 47; Bhagavantam, S., *Ind. Jour. Phys.*, 1933, **8**, 197; Veerabhadra Rao, A., *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 274; Gross, E., and Vuks, M., *Jour. de Phys. et la Rad.*, 1934, **67**, 130; Sirkar, S. C., *Ind. Jour. Phys.*, 1936, **10**, 75.

<sup>2</sup> Bhagavantam, S., *Ind. Jour. Phys.*, 1933, **8**, 197.

<sup>3</sup> Gross, E., and Vuks, M., *Nature*, 1935, **135**, 100, 431 and 998; *Jour. de Phys. et la Rad.*, 1936, **7**, 113.

Rayleigh line in the liquids is only due to the broadening of these new rays and not due to any rotational Raman effect in liquids.

While agreeing with the latter authors as to the existence of quasi-crystalline groups in liquids, Bhagavantam<sup>4</sup> has, however, emphasised that the new lines observed in the organic crystals as well as the wings in the liquid state are present prominently only in optically anisotropic media and owe their origin to the hindered rotation of molecules in the crystals as contemplated by Pauling<sup>5</sup> and not to the vibrations of the crystal lattice.

An entirely different interpretation of the results of Gross and Vuks has been put forward by Sirkar<sup>6</sup> who has investigated this problem specially with a view to determine the true nature of the oscillations giving rise to these lines in crystals. He finds that these lines persist in some cases in solution and their relative intensities and frequency shifts change also with temperature. He concludes therefrom, that they are caused by intermolecular oscillations in polymerised groups of molecules and do not furnish evidence for the persistence of quasi-crystalline groups in liquids. He believes that the wing observed in liquids is an entirely independent phenomenon arising from the rotation of molecules in them.

The subject is thus, of great interest for the proper understanding of the liquid state. The present paper gives a discussion of the results obtained with sulphur and phosphorus in the region of the unmodified line.

## 2. *Experimental.*

In order to investigate the region under consideration, 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 in the present investigation by using carefully distilled liquids of sulphur and phosphorus as described in the first part. Phosphorus was allowed to solidify to a uniform mass and reflection was further minimised by carefully screening about half an inch of the substance near the observation end of the tube from the incident light. Pure crystals of rhombic sulphur formed by slow evaporation from a filtered solution in carbon disulphide were used. Monoclinic crystals were prepared by allowing molten sulphur to cool slowly to 110° C. and maintaining it at that temperature throughout the exposure. The rest of the experimental arrangement was the same as before. Though it would be of great interest to examine the behaviour of the wings at higher temperatures, the darkening of the colour in sulphur and the rapid conversion of

<sup>4</sup> Bhagavantam, S., *Proc. Ind. Acad. Sci.*, A, 1935, 2, 63.

<sup>5</sup> Pauling, L., *Phys. Rev.*, 1930, 36, 430.

<sup>6</sup> Sirkar, S. C., *Ind. Jour. Phys.*, 1936, 10, 109 and 189.

yellow phosphorus to red at higher temperatures prevented a proper investigation to be satisfactorily carried out.

### 3. Results and Discussion.

(a) *Sulphur*.—The sharp and fairly intense Raman line observed at  $88\text{ cm.}^{-1}$  both as Stokes and anti-Stokes in the rhombic sulphur appears weakly in the monoclinic crystals at  $110^\circ\text{ C.}$ , but slightly displaced to  $80\text{ cm.}^{-1}$ . This line becomes weak and diffuse in the liquid and has a frequency shift of  $80\text{ cm.}^{-1}$  and is completely depolarised. As mentioned in the earlier communications, the other lines of rhombic sulphur appear without any change in frequency, intensity or sharpness in the other states also. In the solution in carbon disulphide the line at  $88\text{ cm.}^{-1}$  is masked by the broad wing of the solvent and could not, therefore, be observed. From its non-appearance in the solution in carbon disulphide Krishnamurti<sup>7</sup> concluded that it belongs to the symmetrical oscillations of the  $S_{16}$  group. Liquid sulphur<sup>8</sup> contains only  $S_8$  molecules and the fact that it appears in it as a depolarised band precludes its assignment to the inter-molecular oscillations of polymerised groups of  $S_{16}$  molecule. Since it undergoes changes in frequency, intensity and sharpness in passing to the liquid state, it is highly improbable that it could belong to the inner vibrations of the molecule. It is thus, to be concluded that the line at  $88\text{ cm.}^{-1}$  is to be attributed to the degenerate vibrations of the crystal lattice which persists also in the liquid. According to Lindemann<sup>9</sup> sulphur has a lattice frequency of  $3 \times 10^{12}$  vibrations per second which in wave-numbers gives  $100\text{ cm.}^{-1}$ . His formula connecting the melting point and the lattice frequency is strictly applicable only to cubic lattices and the difference between the calculated and the observed values is evidently due to a difference in crystal structure. If we bear in mind that the density of the monoclinic and the liquid sulphur at  $115^\circ\text{ C.}$  is less than that of rhombic at room temperature, the observed changes in frequency due to variations in density are in a direction which could be expected from the expression given by the latter author. But to calculate the coefficients of expansion of the crystal from the observed changes in frequency with temperature on the assumption that the formula holds good to a first approximation to crystal lattices other than the cubic as has been done by Sirkar<sup>10</sup> for naphthalene, is without justification and any conclusion regarding the nature of such oscillations based upon such calculations has but little significance.

<sup>7</sup> Krishnamurti, P., *Ind. Jour. Phys.*, 1930, 5, 105.

<sup>8</sup> Ephraim, *Anorganische Chemie*, Steinkopff, Dresden and Leipzig, 1934.

<sup>9</sup> Lindemann, F. A., *Phys. Zeit.*, 1910, 11, 609.

<sup>10</sup> Sirkar, S. C., *Ind. Jour. Phys.*, 1936, 10, 114.

(b) *Phosphorus*.—Besides the three vibration frequencies, the Rayleigh line in liquid phosphorus is accompanied on either side by a completely depolarised wing. Its intensity starts from a maximum at 5461 A.U. and ends rather abruptly at a distance of about 70  $\text{cm}^{-1}$  on either side. Under very careful conditions of experimentation it is observed that the wing is replaced in the solids by a fairly sharp intense line displaced from the exciting line by 36 wave-numbers. As may be seen from the accompanying plate the anti-Stokes line is more clearly separated than the Stokes from the exciting line.

In the earlier part, it has been pointed out that the Raman effect and the electron diffraction measurements indicate that phosphorus molecule  $\text{P}_4$  possesses a perfectly tetrahedral structure. In spite of the fact that such a molecule is *optically isotropic*, it is surprising that a completely depolarised wing should accompany the Rayleigh line. The author has also measured the depolarisation of light scattering\* in dust-free liquid phosphorus and obtained a value of about 10% which is unexpectedly high for optically symmetrical molecules. A similar observation has been made by previous workers for carbon tetrachloride. These two facts, namely, the occurrence of the wing in Raman scattering and the finite value of depolarisation in Rayleigh scattering in liquid phosphorus, have presumably the same origin as the sharp line at 36  $\text{cm}^{-1}$  in the solid. The existence of a polymer higher than  $\text{P}_4$  is not known for phosphorus and hence the alternative suggestion that this line may belong to intermolecular oscillations of polymerised groups is out of question.

Since phosphorus crystallises in the cubic system, we can with justification apply the modified formula of Lindemann<sup>11</sup> for the calculation of the frequency of vibration of the crystal lattice. The formula gives  $\omega = C R^{1/2} N^{1/3} \sqrt{\frac{T_m}{MV\frac{2}{3}}}$  where for cubic crystals  $C = 2.75$ ,  $R^{1/2}N^{1/3} = 0.77 \times 10^{12}$  units,  $T_m$  the melting point,  $M$  is the molecular weight and  $V$  is the molecular volume. Taking into consideration the fact that the lattice consists of  $\text{P}_4$  molecules we have  $T_m = 317$ ,  $M = 124$  and  $V = 70.66$  and get  $\omega = 8.2 \times 10^{11}$  vibrations per second or  $\Delta\nu = 27.3 \text{ cm}^{-1}$ . The fairly good agreement between the calculated value and the observed shift is not fortuitous and clearly indicates that this low frequency owes its origin to the degenerate vibrations of the crystal lattice. The crystals persist in the liquid and the broadening of the line gives rise to the depolarised wing.

\* The author's thanks are due to Mr. R. S. Krishnan for kindly permitting the use of his experimental outfit for this work.

<sup>11</sup> Lindemann, F. A., *loc. cit.*; see also Gruneisen, E., *Ann. der Phys.*, 1912, 39, 257.

The above results with sulphur and particularly phosphorus suggest that the low frequency lines that have been observed by Gross and Vuks and recently by Sirkar<sup>12</sup> have their origin in the vibrations of the crystal lattice. While the previous observations by the latter authors were restricted mostly to organic molecules whose structures are far from being simple, the well-known crystal structure and state of molecular aggregation of phosphorus exclude the possibility of interpreting the lines as due to hindered rotation of solid molecules or intermolecular oscillations of higher polymers. But in view of the fact that the wing in the liquids like benzene also appears in the vapour state, the latter could not be explained as mainly due to lattice vibrations; but the superposition of the rotational Raman scattering on the spread-out lines due to the crystal lattice in liquids is responsible for the observed distribution of intensity in the wings. It is also possible that in the case of some substances, Raman lines due either to hindered rotation or to polymerisation or both as well as due to the inner vibrations of molecules may fall in the neighbourhood of the Rayleigh line and every such line has to be examined carefully before any assignment could be made.

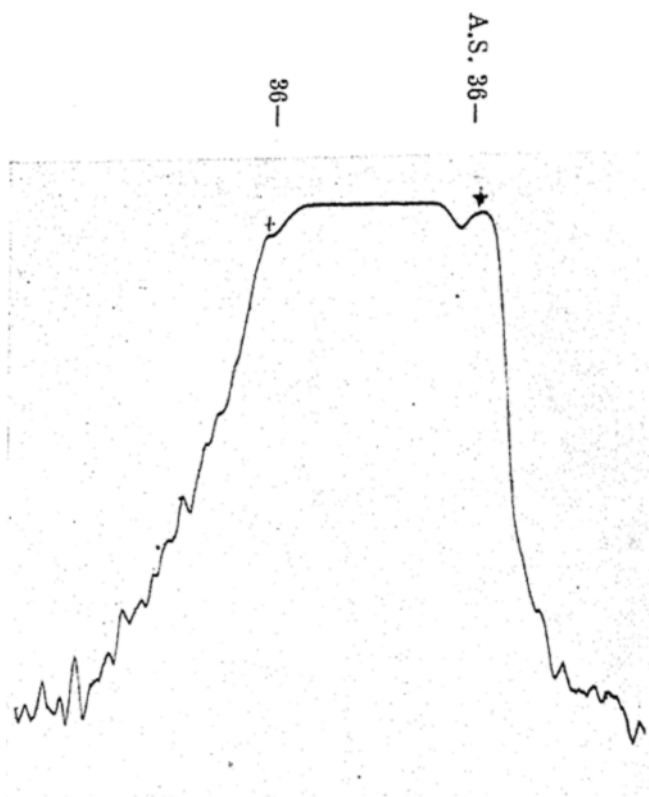
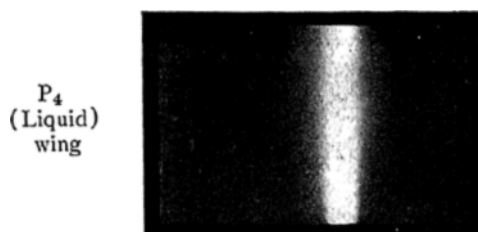
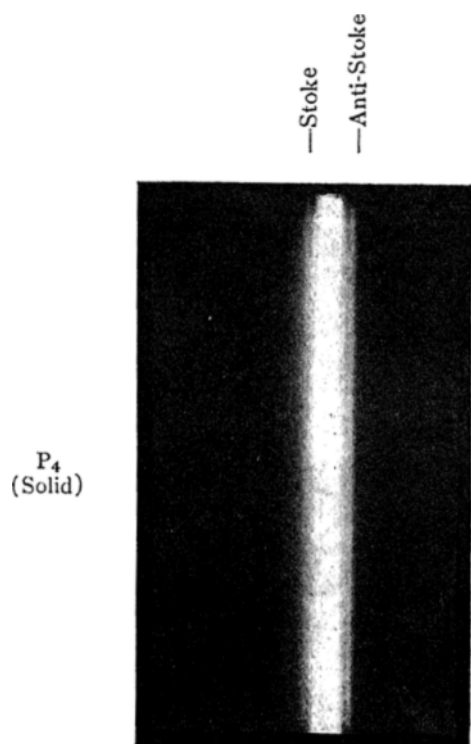
In conclusion, it is my desire to thank Sir C. V. Raman for his keen interest in the work.

*Summary.*

The existing theories regarding the origin of the discrete Raman lines in the solids in the place of the wings accompanying the Rayleigh line in liquids are reviewed. An intense sharp line at  $36 \text{ cm.}^{-1}$  has been reported for solid phosphorus which broadens to a depolarised wing in the liquid state. This frequency agrees well with the frequency of vibration of the crystal lattice calculated from the melting point of phosphorus and therefore, owes its origin to the latter. The Raman line at  $88 \text{ cm.}^{-1}$  observed for rhombic sulphur appears as a weak diffuse depolarised line in liquid sulphur at  $80 \text{ cm.}^{-1}$  and is also attributed to lattice vibrations. The objections for assigning these lines either to Pauling rotation or to intermolecular oscillations of polymerised groups are indicated.

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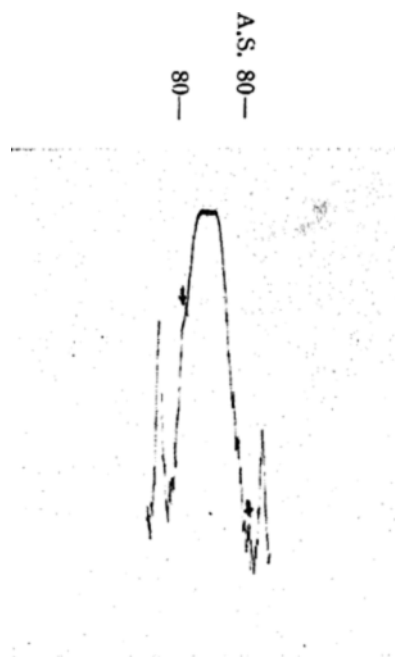
<sup>12</sup> Sirkar, S. C., *Ind. Jour. Phys.*, 1936, 10, 189.



Microphotometric Curve of Solid Phosphorus.



Rhombic Sulphur.



Liquid Sulphur.

Lattice Oscillations.