

THE RAMAN SPECTRA OF SULPHUR AND PHOSPHORUS.

Part I. Polarisation and Molecular Structure.

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1. Introduction.

SULPHUR and phosphorus are two common elements whose molecular structures have not been definitely determined till now. Sulphur, particularly, is interesting in view of the fact that it is known to possess certain properties which are apparently mutually contradictory in the light of the present-day knowledge regarding molecular phenomena. Thus, rhombic sulphur consisting of S_8 molecules¹ yields a large number of absorption bands in the infra-red^{2,3} which suggests the existence of at least an induced electric moment between the neighbouring atoms in the molecule. This is contradicted by the fact that no electric moment⁴ has been hitherto observed for this substance. The Raman spectrum⁵ of crystals of rhombic sulphur yields four intense and three weak lines whose frequency shifts correspond fairly closely with those of the infra-red absorption bands. If we assume with Krishnamurti⁵ that the four intense Raman lines in it are due to the symmetrical oscillations of S_{16} , S_8 , S_4 and S_2 (a view which, however, requires modification) the presence of intense absorption at the corresponding wavelengths appears to be inexplicable. The homopolar nature of the sulphur molecule seems also to be fairly established since no detectable changes in frequency have been observed for the strong Raman lines due to a change from the solid to the liquid condition.⁶ An attempt has been made in this communication to picture a molecular form for sulphur which could explain

¹ Fphraim, *Anorganische Chemie*, Steinkopff, Dresden and Leipzig, 1934.

² Barnes, R. B., *Phys. Rev.*, 1932, **39**, 562.

³ Taylor and Rideal, *Proc. Roy. Soc.*, A, 1927, **115**, 589.

⁴ Rosenthal, S., *Zeit. Physik.*, 1930, **66**, 652 and 657; Dobinski, S., *Bull. Acad. Polonaise*, 1932, A, 239; Curtis, H. J., *J. Chem. Phys.*, 1933, **1**, 247.

⁵ Krishnamurti, P., *Ind. Jour. Phys.*, 1930, **5**, 587; 105.

⁶ Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 120.

qualitatively some of these perplexing facts. It is well known that the polarisation characters of the Raman lines is a sure guide for the determination of the modes of oscillation of the molecule responsible for them. In the present paper the state of polarisation of the Raman lines of sulphur and phosphorus has been studied with particular reference to their molecular structure.

2. *Experimental Arrangements and Results.*

The chief handicap in the investigations on the light scattering in liquid sulphur and phosphorus is the difficulty for obtaining them in a fairly dust-free condition. Even freshly prepared crystals contain large quantities of dust particles which are hard to remove. The method of double-bulb distillation usually employed for ordinary liquids is inapplicable to these high-boiling-point substances due to a strong tendency in them for bumping. In the latter cases the following modification of vacuum distillation is found to work well. The experimental tube is attached to a long cylindrical tube containing the substance and connected to a vacuum pump through the usual drying columns. The distillation is performed either with the pump on or by sealing off the system after thorough evacuation. A small flame is played only *at the top portion of the substance* in the cylindrical tube, keeping the bottom layers comparatively at a low temperature and the liquid distils over slowly into the Raman tube.

During exposure, the substances are kept in a molten condition by placing a heating coil below the experimental tube and the temperature of the substance is maintained at the melting point either by adjusting the distance of the heater from the latter or by regulating the current in it. Direct exposure to the ultra-violet radiations of the mercury arc converts yellow phosphorus to red and deepens the colour of the molten sulphur; in the case of the solution of sulphur in carbon disulphide, colloidal sulphur is precipitated. These vitiating effects of the source are avoided by putting in the path of the incident light a Zeiss yellow glass-filter which transmits the green and the yellow radiations while cutting off the rays upto 4916 A.U. almost completely.

The horizontal and the vertical components of the scattered radiation are separated by means of a large quartz double-image prism and photographed simultaneously on the plate. The state of polarisation of the Raman lines is determined as detailed in a previous paper⁷ after making due allowance for errors of experimentation.

⁷ Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1936, 4, 174.

The results of the investigation are given in Tables I and II and enlarged photographs of the spectra of the two elements are reproduced in the accompanying plates.

TABLE I.
Sulphur.

No.	Infra-red frequency in cm.^{-1} (Barnes)	Raman frequencies in cm.^{-1}						
		Rhombic 25°C.		Mono-clinic 110°C.	Liquid 115°		Solution in CS_2 50%	
		Krishnamurti	Author		Author	ρ	Author	ρ
1	< 77					
2	87(w)	85(m)	88(5)	80(0)	80(2,d)	D	Wing of CS_2	D
3	103(w)	..	114(0)			
4	150(st)	152(st)	152(10)	152(5)	152(10)	D	152(10)	≈ 0.82
5	200—250(st)	183(w)	185(0, d)	..	185(0, d)	..		
6	..	216(st)	216(10)	216(5)	216(10)	P	216(10)	0.23
7	..	243(w)	243(1, d)	..	243(1, d)	
8	267(w)				
9	400(w)	434(w)	434(2, d)	..	434(3d)	D	434(2)	D
10	465(st)	470(st)	468(10)	470(5)	470(10)	P	470(10) 655(st) CS_2	0.08 0.19

st = strong, w = weak, m = medium intensity, d = diffuse.

TABLE II.
Liquid Phosphorus.
Raman frequencies.

No.	$\Delta \nu$ in cm.^{-1}	Intensity	ρ
1	606	10	0.05
2	465	6	≈ 0.87
3	363	2	≈ 0.85

N.B.—D means the depolarisation ratio ρ is equal to or greater than 6/7 and P means that $\rho < 6/7$.

3. Discussion of Results.

(a) *In relation to the molecular structure of Phosphorus.*—According to chemical evidence yellow phosphorus consists of P_4 molecules both in the solid and liquid state. A complete analysis of the crystal structure of yellow phosphorus has not yet been made due probably to the fact that X-rays transform white to the red form.⁸ Natta and Passerini,⁹ however, announced that by cooling the sample to -35°C ., they succeeded in obtaining 22 lines of a cubic pattern. It may, therefore, be reasonable to assume that crystalline yellow phosphorus has a molecular cubic lattice formed of P_4 molecules. The four atoms in the molecule can occupy either the corners of a square or form a regular tetrahedron. Bhagavantam¹⁰ was the first to show that in the Raman effect the former would give four lines while in the latter only three would appear. His investigation¹¹ yielded only three lines in support of a tetrahedral structure for the P_4 molecule. The recent measurements of electron diffraction¹² by phosphorus vapour also rule out the square model and confirm the structure proposed by Bhagavantam. From the identity of the Raman spectra of phosphorus in different states¹³ it is to be concluded that the molecular form remains unchanged upto 450°C .

It was not, however, possible to obtain a good spectrogram for phosphorus in the previous work due to the rapid conversion of the yellow to the opaque red variety. In the present investigation, an intense spectrum has been obtained for the distilled liquid and the carefully cooled solid, where the faint line at 360 which was reported as doubtful in the earlier paper has come out with medium intensity. Except one near the Rayleigh line whose origin will be discussed in the second part, no other line has appeared in the spectrum, which is the result to be expected from the dynamics of the tetrahedral molecule.

The strong and sharp line at 606 is highly polarised and therefore, belongs to the breathing frequency of the tetrahedron. The lines at 465 and 363 are both diffuse and depolarised to an extent of $6/7$ in accordance with the fact that they owe their origin to the two degenerate vibrations. Microphotometric measurements of intensities of the lines are in the ratio $10 : 6 : 2$. The valence force f , between P — P as calculated from the relation $\omega = 2\pi \sqrt{\frac{4f}{m}}$ is 1.64×10^5 dynes per cm.

⁸ Jung, *Centralblatt. f. Min. u. Geol.*, 1926, 107-114.

⁹ Natta and Passerini, *Nature*, 1930, 125, 707.

¹⁰ Bhagavantam, S., *Ind. Jour. Phys.*, 1930, 5, 73.

¹¹ Bhagavantam, S., *Ibid.*, 1930, 5, 35.

¹² Maxwell, Hendricks and Mosley, *Jour. Chem. Phys.*, 1935, 3, 699.

¹³ Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, 2, 260.

(b) *In relation to the molecular structure of Sulphur.*—From the X-ray studies of rhombic sulphur Mark and Wigner¹⁴ concluded that the unit cell contains 128 atoms grouped as eight molecules of 16 atoms each. To explain the strong infra-red absorption observed for sulphur, Taylor and Rideal¹⁵ assumed this structure to be correct and postulated that the S_{16} molecule consists of 8 (S_2) groups which are situated at the corners of a cube. They further believed that the S atoms forming the S_2 groups possess a pseudo-hetropolar binding and have an induced electric moment equivalent to 0.7 times the electric moment it would have if one electron had actually been transferred from one sulphur atom to the other. But recently the structure of rhombic sulphur has been re-determined by Warren and Burwell¹⁶ and they have concluded that it belongs to the Space group V_h^{24} (Fddd) with sixteen S_8 molecules in the unit cell. They have pointed out that each molecule containing 8 atoms of sulphur assumes a symmetrical puckered ring which is made up of two squares one turned 45° with respect to the other (Fig. 1). The planes of the two squares are separated by 1.15 A.U.,

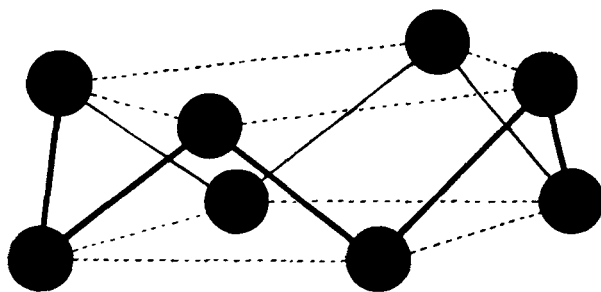


FIG. 1.

Sulphur Molecule. Unbroken lines indicate co-valent bonds and the dotted lines co-ordination bonds.

the side of the square is 3.38 A.U. and the valence angle is 105° . This structure has found good support from the measurements of magnetic susceptibility* along the three axes of the crystals of rhombic sulphur.

The structure given by Warren and Burwell, however, does not explain the strong infra-red absorptions of sulphur which depend only on the change in the electric moment during the vibrations of the molecule. For this purpose, we assume that the neighbouring atoms in the plane of each

¹⁴ Mark and Wigner, *Zcit. Phys. Chem.*, 1924, 111, 398.

¹⁵ Taylor and Rideal, *loc. cit.*

¹⁶ Warren, B. E., and Burwell, J. T., *Jour. Chem. Phys.*, 1935, 3, 6.

* Unpublished work of Mr. P. Nilakantan of this laboratory.

square are co-ordinately linked and hence they possess virtually opposite charges which in absorption act as electric dipoles (Fig. 2). This assumption

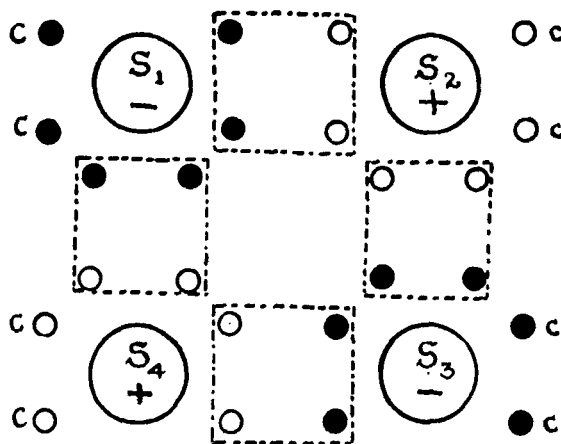


FIG. 2.

The electrons within the dotted square are linked with co-ordination bonds.

is justified for the following reasons. If we consider the four sulphur atoms S₁, S₂, S₃ and S₄ in the plane of one of the squares, each atom has six electrons in the outer shells of which two marked *c* are shared co-valently with two atoms in the other square. In the absence of any other bond, the octet of each of the eight atoms in the molecule is completed and the sulphur is di-valent. But we know that in the case of sulphur, the outer shell can expand to ten electrons as in sulphur tetrachloride and twelve electrons as in sulphur hexafluoride. In fact, Bassett and Durrant¹⁷ assume that the chromogenetic properties of sulphur are to be attributed to the S atoms possessing a ten-electron sheath. Therefore, the two pairs of unshared electrons of the atoms S₁ and S₃ (Fig. 2) are co-ordinated with those of the neighbouring atoms S₂ and S₄ with the result that S₁ and S₃ possess twelve and S₂ and S₄ possess only eight electrons in their outer shells. This is equivalent to attributing a positive charge to S₂ and S₄ and a negative charge to S₁ and S₃ and the atoms become quadrivalent. The same is true of the units of the other square. From the geometry of the molecule it follows that no permanent electric moment could be discovered for the element.

Now we shall examine how far the Raman and the infra-red measurements lend support to the above molecular structure. A molecule with 8 atoms as in sulphur has eighteen normal vibrations out of which by reason

¹⁷ Bassett, H., and Durrant, R. G., *J. C. S.*, 1927, 1401.

of symmetry some may be forbidden in the Raman effect and some may be degenerate. In rhombic sulphur eight Raman lines have been recorded including a new line at 114 which coincides with the infra-red absorption at 103. Three of these are very intense, one is of medium intensity and the rest are weak and diffuse. The line at 88 alone suffers characteristic changes in frequency, intensity and sharpness in passing to the liquid state.

Of the three intense lines the one at 470 is almost completely polarised and the line at 216 possesses a low depolarisation ratio. These two, therefore, belong to the totally symmetrical oscillations of the molecule. From Fig. 1 it is clear that the two possible symmetrical vibrations are (1) that in which the two squares are vibrating against each other, (2) that in which the four atoms in each square move towards or away from the centre of the square. The first mode of oscillation taking place in a direction parallel to the symmetry axis involves no change in the electric moment and should therefore be inactive in the infra-red. The second mode of oscillation which is perpendicular to the axis introduces changes in the electric moment due to the change in the distance between the units of the dipole as contemplated by co-ordination and therefore would give rise to absorption in the infra-red. The infra-red measurements, however, show that there is a marked absorption at points corresponding to both these frequencies; but while the absorption is pretty sharp at about 470, it is extended over 50 wave-numbers at 216. As Barnes¹⁸ himself remarks this latter region if explored by a finer grating would undoubtedly reveal finer structures. In the Raman effect, this line is accompanied on both sides by two faint and diffuse lines at 183 and 243. Due to their extreme weakness the state of polarisation of these lines could not be determined. It is only reasonable to assume that the strong absorption is due to anti-symmetric oscillations giving rise to these faint lines and does not have the same origin as the strong, sharp and well-polarised line at 216. Thus the line at 216 is to be attributed to the oscillations of the squares against each other. Wagstaff¹⁹ calculates the atomic frequency of sulphur according to Einstein's formula $\nu = 2.54 \times 10^7 \frac{V^{1/6}}{k^{1/2}M^{1/2}}$ where k = compressibility, V = atomic volume and M = atomic weight and gets a value 7.3×10^{12} vibrations per second, which in wave-numbers gives 243. If we consider the oscillations of the squares against each other as akin to an atomic vibration, the proximity of the observed frequency 216 to the calculated value 243 lends further support to the above assignment.

¹⁸ Barnes, *Loc. cit.*

¹⁹ Wagstaff, J. E. P., *Phil. Mag.*, 1924, 47, 84.

The intense, sharp and polarised line at 470 is consequently to be attributed to the expansions and contractions of the squares constituting the molecule. As a first approximation, neglecting for a moment the influence of the atoms of one square over those of the other, the frequency corresponding to this oscillation is given by $\omega = \frac{1}{2\pi} \sqrt{\frac{2f}{m}}$.²⁰ If we further assume that the force between the neighbouring atoms along the side of the square is very nearly the same as for phosphorus, namely about 1.75×10^5 dynes per cm., the calculated frequency comes to about 485. Involving as it does, great approximations and assumptions, the agreement between the calculated and the observed values justifies, to some extent, the assignment of the line to the expansions and contractions of the square.

The third line at 150 is depolarised to an extent of 6/7 and is presumably to be attributed to the torsional oscillations of the two squares against each other. The strong infra-red absorption observed at 150 evidently owes its origin to the same mode of oscillations of the molecule. The marked intensity and sharpness of a completely depolarised vibration is, however, surprising. The weak line at 434 is also completely depolarised and cannot therefore be considered as the overtone of 216. This line as well as the absorption at 400 is probably due to one of the anti-symmetric degenerate vibrations of the atoms in each square. The origin of the depolarised line at 88 will be discussed in the next paper.

It will be interesting to see how far the molecular structure proposed above could explain the physical properties of sulphur. It is well known²¹ that when sulphur is heated it melts at 115° C. to form a brownish yellow transparent mobile liquid and as the temperature rises to about 220° C. it becomes more and more viscid and dark reddish brown in colour. At temperatures higher than 250° C. it attains a greater transparency and fluidity. On quenching the viscid liquid between 220°–250° C. in cold water a soft plastic product is obtained which after distension to four times its length regains its original form. If the liquid above 400° C. is poured in a thin stream into liquid air, it can be obtained as a fine thread of diameter 0.5–1 mm. This has an extraordinary elasticity at room temperature extending to 5.5 times its original length without passing its elastic limits. This elasticity is lost in half an hour.

On the basis of the structure proposed here, the presence of the co-ordinate bond between the neighbouring atoms in the plane of the square may

²⁰ Bhagavantam, S., *Ind. Jour. Phys.*, 1930, 5, 73.

²¹ Mellor, J. W., *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 10, 43.

be considered as a barrier for the interpenetration of the molecules upto the melting point. As the temperature is raised, this bond of co-ordination which is weak, gradually gives way and the molecules are free to approach nearer as shown in Fig. 3. This transition may be assumed to take place

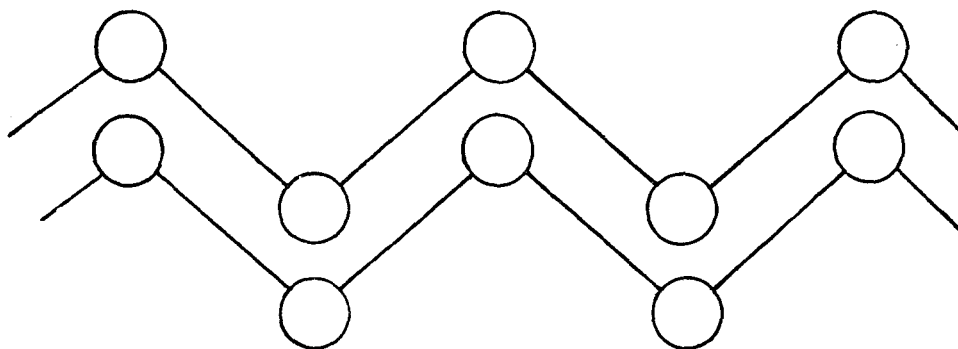


FIG. 3.

Showing the closer approach of two neighbouring molecules.

at about 160° C. which is the transition point at which the increase of viscosity begins. The process is to be considered as equivalent to polymerisation and accounts satisfactorily for the darkening of the colour and it is, therefore, unnecessary to postulate the formation of thiozone S_3 as has been proposed by Erdmann.²² Any sudden cooling of the liquid at this stage gives a temporary setting to the interlocked puckered rings which would, as is to be expected, possess the great elasticity that has been observed in plastic sulphur. At temperatures near the boiling point of sulphur, the ring itself may break open and the staggered chains thus formed are capable of yielding the fine highly-elastic strings by sudden cooling to the temperature of liquid air. Finally, on boiling, the chain can be expected to break up further giving rise to double-bonded $S = S$ molecules.

In conclusion the author desires to express his heartfelt thanks to Prof. Sir C. V. Raman for his inspiring interest in the work.

Summary.

The polarisation of Raman lines of sulphur and phosphorus is investigated with reference to their molecular structures. An intense Raman spectrum of liquid phosphorus has yielded three lines the state of polarisation of which conforms to the Raman-active vibrations of a tetrahedral molecule. The molecule of sulphur is considered to be a symmetrical puckered ring made up of two squares of four atoms each, one square placed at 45° with

²² Erdmann, H., *Liebig's Ann.*, 1908, 362, 133.

respect to the other. To explain the strong infra-red absorptions, the neighbouring atoms in the plane of each square are assumed to be connected with co-ordination bonds which give rise to electric dipoles causing absorption. The two lines 470 and 216 which are well-polarised are assigned to two symmetrical oscillations of such a model, 470 to the vibration in which the four atoms in each square move towards or away from the centre of the square and 216 to the vibration in which the two squares move towards or away from each other. The lines at 150 and 434 are completely depolarised and belong to anti-symmetric vibrations. The well-known changes of sulphur on heating are explained on the basis of this new molecular structure. A method of distilling high-boiling-point substances is also described in the paper.