

# THE RAMAN SPECTRUM OF PHOSPHORUS.

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Received August 23, 1935.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

## 1. Introduction.

BHAGAVANTAM<sup>1</sup> investigated the Raman effect with yellow phosphorus in the solid state using the green and yellow radiations of the mercury arc as the exciting lines. He gives the characteristic frequencies as 607 (6), 468 (3) and 374 (1); the figures in the brackets being the intensities as recorded with the 5460 Å. U. excitation. He has discussed his results theoretically,<sup>2</sup> considering the two alternate forms for the tetra-atomic molecule, namely, that of a square and of a tetrahedron respectively. The former model would give four different frequencies of oscillation, while the tetrahedron would give three frequencies: Accordingly, the experimental results are regarded as supporting the tetrahedral model for P<sub>4</sub> which is in agreement with the fact that the yellow phosphorus crystallises in the cubic system.<sup>3</sup> For the particular law of forces adopted, the frequencies should have the ratio 2:√2:1; the fact that the observed frequencies deviate from this ratio is regarded as indicating that the force system in the molecule is more complicated than that assumed. In the present paper the Raman spectrum of yellow phosphorus has been critically studied with the substance in four different states: (1) vapour, (2) liquid, (3) solid and (4) solution in carbon disulphide. Such a comparative study is evidently of interest in order to ascertain the influence of the state of aggregation on the characteristic frequencies of the molecules, and has so far been made in the case of very few substances. In the present investigation, some additional bands have been recorded besides those reported by Bhagavantam and a small shift has been observed in the frequency of the most intense line as we pass from the solid to the liquid and to vapour.

## 2. Experimental Arrangements and Results.

The experimental arrangements were the same as those described in the previous communications of the author<sup>4</sup> in these *Proceedings*. Small

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<sup>1</sup> Bhagavantam, S., *Ind. Jour. Phys.*, 1930, 5, 35.

<sup>2</sup> Bhagavantam, S., *Ind. Jour. Phys.*, 1930, 5, 73.

<sup>3</sup> Natta and Passerini, *Nature*, 1930, 125, 707.

<sup>4</sup> Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, 1935, 1, 850.

transparent pieces of yellow phosphorus were kept immersed in distilled water and exposed in the vertical tube, the solid being kept at the room temperature by the circulation of cold water in an outer jacket surrounding the experimental tube. Liquid phosphorus was formed by the heating of the yellow crystals contained in an evacuated tube, by the heat of the mercury arc itself. The solution in carbon disulphide was prepared by dissolving clean pieces of yellow phosphorus in freshly distilled carbon disulphide contained in a closed tube during exposure. The arrangement for the vapour is shown in Fig. 1. A few bits of phosphorus were contained in a thick-

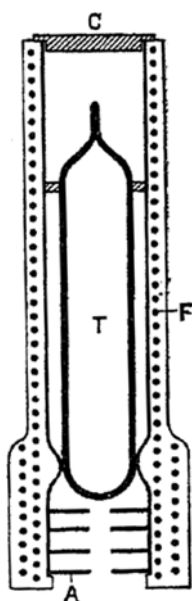


FIG. 1. T=Tube, F=Furnace, A=Aperture, C=Cap.

walled pyrex tube, which was evacuated, rendered moisture free, and sealed off. The tube was supported vertically as illustrated, inside another tube over which nichrome wire was wound in order to serve as an electric furnace. A few additional turns of heating coil at the lower end of the furnace prevented the condensation of the vapour in the bottom of the tube. Once the phosphorus was vaporised, it was found necessary to keep the temperature high enough in order to prevent the formation of red phosphorus. With a current of about 4.5 amperes in the heating coil, the temperature inside the tube remained almost steady at 450° C. A series of apertures were used on the observation side so that the reflection from the walls of the tube was completely eliminated.

The time of exposure was four hours for the solid, twelve hours for the liquid and the solution and six days for the vapour at a pressure of about 15 atmospheres. The spectrograms were measured with a Hilger Cross-Slide

Micrometer in comparison with an iron arc spectrum which was recorded in the centre of every plate.

TABLE I.  
*Solid Phosphorus (Temperature 30° C.).*

Exciting line	Raman lines		$\Delta\nu$ in cm. <sup>-1</sup>	Intensity
	$\lambda$	$\nu$		
5790.5 ( $\nu = 17265$ )	6000.0	16662	603	3
„	5950.6	16800	465	1
5769.6 ( $\nu = 17328$ )	5977.5	16725	603	3
„	5928.3	16864	464	1
5460.7 ( $\nu = 18308$ )	5646.0	17706	602*	8
„	5602.2	17845	463	4
„	5573.3	17938	370(?)	0
4358.3 ( $\nu = 22938$ )	4476.0	22335	603	2
„	4447.9	22477	461	1

\* This line is followed by an unresolved wing.

TABLE II.  
*Liquid Phosphorus (Temperature 75° C.).*

Exciting line	Raman lines		$\Delta\nu$ in cm. <sup>-1</sup>	Intensity
	$\lambda$	$\nu$		
5790.5	6001.5	16659	606	6
„	5951.6	16800	465	3
5769.6	5979.0	16720	606	6
„	5928.6	16863	465	3
5460.7	5647.4	17702	606	8
„	5602.5	17844	464	4

TABLE III.  
Phosphorus Vapour (Temperature 450° C.).

Exciting line	Raman lines		$\Delta\nu$ in $\text{cm.}^{-1}$	Intensity
	$\lambda$	$\nu$		
5460.7	5649.5	17696	612	3
„	5603.0	17843	465 (diffuse)	1

TABLE IV.  
Solution in CS<sub>2</sub> (52%).

Exciting line	Raman lines		$\Delta\nu$ in $\text{cm.}^{-1}$	Intensity
	$\lambda$	$\nu$		
5460.7	5664	17650	658	3
„	5649	17697	611	8
„	5603	17843	465	3

In addition to the lines tabulated above, a strong fluorescent band has also been recorded in all the four plates with its centre at 6400 Å. U. and extending from 6230 Å. U. to 6550 Å. U., which is evidently due to the phosphorus itself. The strong line at 602 in the solid is accompanied by a faint wing to the red side, which would probably resolve into a companion line at higher dispersions. The faint line at 374 reported by Bhagavantam<sup>5</sup> has appeared only as a faint darkening on the plates of the solid and the liquid and the author is, hence, unable to confirm the reality of that line.

The influence of change of state on the Raman lines is not shown to any marked extent. The line at 602 in the solid is shifted slightly towards a higher frequency while passing from the solid to the liquid and hence to the vapour, the variation in frequency being of the order of four wave-numbers from the solid to the liquid and six wave-numbers from the liquid to the vapour. The shift remains almost the same in the two states of the vapour and the solution. The line at 464 appears unshifted in all the four states ;

<sup>5</sup> Bhagavantam, S., *Loc. cit.*

but in the case of vapour it has become slightly more diffuse. Only small variations in the frequency have been observed in the past in the case of the non-polar compounds like  $H_2$  or  $O_2$ ,<sup>6</sup> while the polar molecules like hydrochloric acid<sup>7</sup> give in general large shifts. In the case of sulphur, the author<sup>8</sup> has not been able to observe any change in the frequencies from the solid to the molten conditions. Hence we are led to conclude that the small shifts observed in phosphorus while passing from the solid to the vapour are only such as could be accounted for by the Lorentz-Lorentz forces and shows that the  $P_4$  molecule is non-polar. It may also be of interest to mention that though the frequency shifts in the vapour and solution are almost identical, the spectrum of carbon disulphide itself is comparatively feeble.

In conclusion the author wishes to thank Prof. Sir C. V. Raman for his kind interest in the work.

*Summary.*

The Raman spectrum of yellow phosphorus as vapour, liquid, solid, and solution in carbon disulphide has been obtained. Only small changes in frequency are observed while passing from solid to liquid and to vapour, indicating the non-polar character of the molecule. The spectrum of carbon disulphide is rendered weak although the spectrum of phosphorus in solution comes out strongly. A strong fluorescent band extending from 6230 Å. U. to 6550 Å. U. has also been recorded in all cases.

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<sup>6</sup> Kohlrausch, *Der Smekal-Raman Effect*, 1931, p. 126.

<sup>7</sup> Callihan and Salant, *Jour. Chem. Phys.*, 1934, 2, 317.

<sup>8</sup> Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, 1934, 1, 120.