

RAMAN SPECTRUM OF SULPHUR IN THE SOLID AND LIQUID STATES.

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1. Introduction.

DR. P. KRISHNAMURTI¹ examined the Raman spectrum of rhombic sulphur with the 5461 Å mercury line and observed three strong lines with wave-numbers $\nu_1 = 152$, $\nu_2 = 216$ and $\nu_3 = 470$ and three other faint lines $\nu_0 = 85$ (anti-stokes), $\nu_4 = 243$ and $\nu_5 = 434$. Considering the three strong lines as giving the three fundamental frequencies of the sulphur complex, he explained the bands of high frequency found by Taylor and Rideal² in absorption as overtones and combinations of the fundamentals. All these frequencies were found by Barnes³ to correspond fairly well with the absorption bands of sulphur in the remote infra-red. Barnes, however, found that there were other absorption bands at 130μ , 96μ and 37.5μ for which there are no corresponding Raman lines. Dr. Krishnamurti also studied the Raman spectrum of a concentrated solution of sulphur in carbon disulphide and found three lines in approximately the same positions as the strong lines in the crystal. He, however, reported a disappearance of the anti-stokes ν_0 in the solution and small changes of about 3 wave-numbers in ν_1 and ν_2 .

As Dr. Krishnamurti had not examined the case of molten sulphur, it was thought worth while to study it and compare the results with those for solid sulphur.

2. Experimental Procedure.

It has been shown by Dr. Krishnamurti⁴ that while the intense green line of the cadmium arc gives all the sulphur lines strongly, the red radiations excite them only very feebly. Since molten sulphur absorbs the green radiations, a suitable source for the excitation of the Raman spectra of both the liquid and solid phases was found in the intense yellow doublet of the sodium lamp. The lamp made use of in the following investigations

¹ Krishnamurti, *Ind. J. Phys.*, 1930, 5, 105.

² Taylor and Rideal, *P.R.S. (A)*, 1927, 115, 589.

³ R. B. Barnes, *Phys. Rev.*, 1932, 39, 562.

⁴ Krishnamurti, *Ind. J. Phys.*, 1930, 5, 587.

was supplied by the firm of Carl Zeiss and gave a few faint lines besides the prominent yellow doublet.

The rhombic crystals of sulphur were prepared fresh from a solution of sulphur in carbon disulphide and placed in a rectangular cell. The cell was illumined by two lamps on either side and the scattered light proceeding from a small circular aperture on the third side was photographed by a Fuess glass spectrograph. An exposure of about two hours was sufficient for giving a good spectrogram for sulphur crystals, using Agfa "Superpan" films (Speed H & D 2000). For the investigations with liquid sulphur, a pyrex tube $\frac{3}{4}$ " in diameter was closed at one end and surrounded by a heating coil of about 30 ohms. The tube was heated to a temperature of about 115°C. and molten sulphur was poured into it and was maintained in the liquid condition by the proper adjustment of the current in the heating coil. Raman lines of the same intensity as those of the rhombic crystals were obtained only after an exposure of about 48 hours.

3. Results and Summary.

The Raman lines appeared as double lines corresponding to the double lines used for excitation and hence were easy of identification. The three strong lines observed by Dr. Krishnamurti¹ were recorded as intense lines, but the fainter lines did not appear even after long exposures. No difference was observed between the structure or positions of the lines in the liquid state and those of the crystalline form. Hence the liquid state appears to differ from the state of solution in which case a very small shift in the frequencies has been recorded. This is in agreement with the conclusions of Taylor and Rideal² from the infra-red measurements that the same complex is responsible for those vibrations which remain unchanged in all phases.

Since the micrometer readings for the liquid and the crystal were the same, only one set of readings was used for computation.

Exciting line 5895.93 ($\nu = 16956$).

Frequency	Raman line ν	$\Delta \nu$		λ in μ	
		Author	Krishnamurti	Raman	Infra-red
ν_1	16806	150	152.2	66.7	67
ν_2	16742	214	216.2	46.7	40-50
ν_3	16489	467	470	21.4	21.5

ν_1, ν_2 also gave intense anti-stokes lines while ν_3 gave a faint one.

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