RAMAN SPECTRUM OF SULPHUR

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Received September 20, 1940
(Communicated by Prof. S. Bhagavantam, M.SC., F.A.SC.)

1. *Introduction*

THE infra-red and the Raman spectra of sulphur do not seem to have received a satisfactory interpretation till now, in spite of the fact that it is a common element. Krishnamurti[1] and Venkateswaran[2] are amongst those who have studied the Raman spectrum of this substance in the crystalline state. There is a fair agreement between the frequencies reported by these two authors as may be seen from Table II. Krishnamurti recorded seven Raman frequencies and Venkateswaran also recorded these and an additional frequency at 114. In all, eight frequencies had thus been recorded and Venkateswaran attributed one of these at 88 to the lattice and the remaining seven to the S_8 molecule. Bhagavantam and Venkatarayudu[3] calculated the normal frequencies of the sulphur molecule and they remarked that the line at 114 may also be attributed to the lattice. If such an interpretation is correct, there should be expected another fundamental at about 500. Their calculations lead to this conclusion.

The infra-red absorption of crystals of rhombic sulphur has been studied by Coblentz,[4] Schubert[5] and Taylor and Rideal[6] in the near infra-red region and by Barnes[7] in the far infra-red region. Krishnamurti has explained the near infra-red absorption maxima as combinations of two or more suitable fundamental frequencies. Venkateswaran attempted to identify all the observed far infra-red absorption maxima with one or other of the frequencies obtained in the Raman effect. Neither of these authors had taken into account the selection rules appropriate to the case of sulphur. It has been shown by Bhagavantam and Venkatarayudu that no correspondence between the infra-red absorption and Raman spectra need be expected in this case and we shall see later that only a limited number of combinations are permitted to appear in its infra-red absorption spectrum. In view of these discrepancies, it becomes necessary to revise the interpretation of the Raman and the infra-red absorption frequencies.

Accordingly, a detailed investigation of the Raman spectrum of a single crystal of rhombic sulphur is undertaken and a more satisfactory explanation of the infra-red absorption maxima is attempted in the present paper.

2. *Experimental*

Crystals of appreciable size have been grown by slow evaporation of a filtered solution of sulphur in carbon disulphide. A small flawless single crystal of rhombic sulphur is selected for the study. Light from a 6-inch quartz mercury arc lamp is condensed by means of an 8-inch glass condenser on to one face of the crystal. The scattered light emerging out from one of the other faces is focussed on the slit of a Fuess glass spectrograph with a suitable lens. With proper precautions, an intense and clear spectrum of sulphur has been obtained by giving an exposure of about twenty hours and this picture is reproduced in the accompanying plate. λ 5461 A.U. is used as the exciting radiation and Ilford Golden Isozenith plates are used to record the spectrum.

3. *Raman Spectrum of Sulphur*

The Raman frequencies obtained with a single crystal of rhombic sulphur are given in Table I.

TABLE I

Raman frequencies of sulphur

Wave-length of the Raman line A. U.	Wave number Cm.$^{-1}$	Exciting line A. U.	Raman shift Cm.$^{-1}$
5485·8	18224	5460·7	84
5495·1	18193	,,	115
5507·4	18152	,,	156
5516·3	18123	,,	185
5526·1	18091	,,	217
5532·7	18069	,,	239
5595·1	17868	,,	440
5606·0	17833	,,	475
5620·1	17788	,,	520
5435·9	18391	,,	− 83
5426·9	18422	,,	−114

$\Delta\nu =$ 84, 115, 156, 185, 217, 239, 440, 475, 520.

The Raman frequencies of rhombic sulphur obtained by the author are compared with those obtained by the earlier workers in Table II. An

TABLE II

Raman frequencies of sulphur compared with earlier observations

Krishnamurti	85 (med. st).	..	152 (*st*)	183 (*w*)	216 (*st*)	243 (*w*)	434 (*w*)	470 (*st*)	..
Venkateswaran	88 (5)	114 (0)	152 (10)	185 (0, *d*)	216 (10)	243 (1, *d*)	434 (2, *d*)	468 (10)	..
Author	84 (5)	115 (5)	156 (10)	185 (1, *d*)	217 (10)	239 (1, *d*)	440 (2, *d*)	475 (7)	520 (0)

extremely faint line at 520 has been recorded here for the first time. The numbers in the brackets represent the relative intensities.

The Raman line at 114 has been recorded by Venkateswaran as a faint line whereas it is quite intense in the author's pictures.

4. *Effect of Temperature*

A rhombic crystal was mounted inside an electric heater provided with suitable windows. The temperature of the crystal was gradually raised to 105° C. where it was kept constant. It is expected, as has been shown by Bech and Ebbinghaus,[8] that the monoclinic variety is obtained in this way at 105° C. The Raman spectrum of sulphur has been photographed under these conditions and also at the room temperature on the same plate by using a Hartmann diaphragm to ascertain whether there is any shift in the lines or not. No change, either in the frequency or in the relative intensities of the Raman lines, could be observed.

Venkateswaran has, however, recorded that the line at 88 of rhombic sulphur is shifted to 80 in the case of monoclinic sulphur at 110° C. Sirkar and Gupta[9] also studied the Raman spectra of rhombic and monoclinic varieties of sulphur but they reported that no change has been observed to take place in the position of the lines with the transformation from the rhombic to the monoclinic variety.

5. *Effect of Crystal Orientation*

In the case of a uniaxial crystal, if we designate the direction of the incident light by OX, that of the scattered light by OY and the vertical line by OZ, three alternatives arise in respect of the nature of the incident light. It may be unpolarized or linearly polarized along OZ or linearly polarized along OY. In each case, the optic axis of the crystal may be placed parallel to either OX or OY or OZ. Thus the number of alternative arrangements becomes nine. For each one of these settings, the scattered light may either be photographed as such or only the horizontal component of it or only the vertical component of it may be photographed, thus enabling the observer to secure 27 separate spectra on the whole. In the case of rhombic sulphur, which is a biaxial crystal, the number will obviously become 54. It may easily be seen that only 24 of these, obtained by analysing both the incident and the scattered beams, are the most important ones. These 24 spectrograms have been obtained by the author in the present investigation with a good crystal of sulphur.

Light from a quartz mercury lamp is focussed on the crystal by a large glass condenser involving a semi-angle of convergence of about 10°. A suitably oriented polaroid disc is used for securing the desired state of polarization for the incident light. The scattered light is separated into the horizontal and the vertical components by means of a suitably oriented double image prism and the two components are simultaneously photographed. On account of the fact that the crystal used is not a big one and that a polaroid has been employed, it is thought that the results obtained cannot be deemed to have a quantitative significance and are not, therefore, extensively quoted here. Only the main features are recorded.

The important conclusions, arrived at after a careful examination of the plates, relate to: (i) the reciprocal behaviour of the total symmetric and the degenerate oscillations and (ii) the existence of two preferred orientations, namely, those in which both the direction of the incident light vector and the orientation of the C-axis are along OZ. In these two cases, the total symmetric oscillations come out very strongly. This is apparently due to the fact that the plane of the sulphur ring is parallel to the C-axis and we have to conclude that the total symmetric oscillations are excited more strongly when the incident light vector is parallel to the plane of the ring than when it is perpendicular to it. The reciprocal behaviour of the total symmetric oscillations on the one hand and the degenerate oscillations on the other is also expected and this result is analogous to the observations made by Nedungadi[10] in $NaNO_3$ and Bhagavantam[11] in calcite.

6. *Discussion of the Raman Spectrum and Infra-red Absorption*

From the X-ray studies of rhombic sulphur, Mark and Wigner[12] concluded that the unit cell contains 128 atoms grouped as eight molecules of sixteen atoms each. Taylor and Rideal extended that view by postulating that the S_{16} molecule consists of 8 (S_2) groups which are situated at the corners of the cube. Contrary to these findings, Warren and Burwell[13] concluded from similar studies that rhombic sulphur belongs to the space group V_h^{24} and that the unit cell contains sixteen S_8 molecules. The atoms in each molecule are located at the corners of a puckered octagon made up of two equal squares one turned through 45° with respect to the other. The planes of the two squares are parallel but not coincident. From the intensity measurements, they found that the plane of the ring is parallel to the C-crystallographic axis and makes an angle of about 50° with the *a*-axis.

Assuming the model suggested by Warren and Burwell, Bhagavantam and Venkatarayudu[14] calculated the normal frequencies of sulphur molecule by applying the group theoretical methods. Out of the eleven vibrational frequencies that are to be expected, only seven are active in Raman effect, three others are active in infra-red absorption and one frequency is inactive in both. Of the nine frequencies obtained by the author, the two at 84 and 115 are now attributed to the lattice and the remaining seven are identified as the fundamental frequencies of the S_8 molecule. The fundamental frequencies obtained by the author are compared with those calculated by Venkatarayudu[15] in Table III.

TABLE III

Comparison between the observed and the calculated frequencies

Number	Class	Frequency calculated Cm.$^{-1}$	Frequency Observed in Raman effect Cm.$^{-1}$	Frequency observed in infra-red absorption Cm.$^{-1}$
ν_1	A_1	470	475	*f*
ν_2	,,	216	217	*f*
ν_3	B_1	400	*f*	400 (*w*)
ν_4	B_2	359	*f*	*f*
ν_5	E_1	456	*f*	465 (*st*)
ν_6	,,	203	*f*	200 (*st*)
ν_7	E_2	482	520	*f*
ν_8	,,	196	185	*f*
ν_9	,,	113	156	*f*
ν_{10}	E_3	454	440	*f*
ν_{11}	,,	243	239	*f*

f denotes that the line is forbidden from appearing. The three fundamental infra-red absorption maxima that are to be expected and that have been observed are also given in the last column of the above table.

Of these, ν_1 and ν_2 come under the total symmetric class and the rest are degenerate. The two possible symmetrical vibrations are (1) that in which the two squares are vibrating against each other and (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 takes place in a direction parallel to the symmetry axis and Venkateswaran has given sufficient reasons to consider the frequency at 217 as the one arising out of such oscillations. Hence, the second one at 475 which is intense, sharp and well polarized, should be attributed to the expansions and contractions of the squares constituting the molecule.

The unit cell of rhombic sulphur contains sixteen molecules of eight atoms each. A complete analysis of its normal modes would be very difficult of achieving. Bhagavantam and Venkatarayudu[16] have shown that when a group of atoms constituting an ion or molecule goes to build up a crystal, its normal modes usually undergo three types of modification, namely, splitting of degenerate vibrations, multiplicity due to the unit cell containing more than one molecule and alteration in selection rules. It is, however, a matter of experimental fact that none of the Raman lines which are forbidden in the case of the sulphur molecule have appeared in the crystal nor has any splitting been observed. We may therefore regard the selection rules applicable to a molecule to be valid in the case of the crystal also both in Raman effect and infra-red absorption.

The character table and the selection rules derived by Bhagavantam and Venkatarayudu in the case of sulphur molecule reveal that only three fundamental frequencies should appear in the infra-red absorption and that there should be no correspondence between the Raman lines and the infra-red absorption maxima. Barnes has studied the infra-red absorption of rhombic sulphur crystal in the far infra-red region and he recorded maxima at < 77, 87, 104, 149, 200–250, 267, 400 and 465. Of these, the three peaks at 149, 200 and 465 are strong absorptions. The three infra-red fundamentals in the case of sulphur have already been taken as 200, 400 and 465. The frequencies at < 77, 87 and 104 can be taken as those due to the lattice. The remaining two frequencies observed by Barnes and also the four maxima observed by Taylor and Rideal in the near infra-red region at 685, 840, 932 and 1289 have to be explained either as overtones or combinations with due regard to the selection rules.

Following the selection rules for the combinations and overtones given by Tisza,[17] a detailed scheme for their appearance or otherwise has been worked out. The selection rules for the overtones in the infra-red absorption are given in Table IV. *f* and *p* denote respectively that the line is forbidden or permitted to appear.

TABLE IV

Selection rules for the overtones in the infra-red absorption of sulphur

Class	Fundamental	First overtone	Second overtone
A_1	*f*	*f*	*f*
A_2	*f*	*f*	*f*
B_1	*p*	*f*	*p*
B_2	*f*	*f*	*f*
E_1	*p*	*f*	*p*
E_2	*f*	*p*	*p*
E_3	*f*	*f*	*p*

The selection rules for the combinations are given in Table V. Combinations which are permitted in the infra-red absorption are printed in bold type. For example, a frequency coming under the class B_1 can combine with one coming under either E_3 or A_1 only. In the former case, the combination will have the characters of the representation E_1 and in the latter it will have those of B_1. Accordingly, these combinations are permitted in the infra-red absorption.

TABLE V

Selection rules for the combinations in the infra-red absorption of sulphur

Class	A_1	A_2	B_1	B_2	E_1	E_2	E_3
A_1	A_1	A_2	$\mathbf{B_1}$	B_2	$\mathbf{E_1}$	E_2	E_3
A_2		A_1	B_2	$\mathbf{B_1}$	$\mathbf{E_1}$	E_2	E_3
B_1			A_1	A_2	E_3	E_2	$\mathbf{E_1}$
B_2				A_1	E_3	E_2	$\mathbf{E_1}$
E_1					$A_1+A_2+E_2$	$\mathbf{E_1}+\mathbf{E_3}$	$\mathbf{B_1}+\mathbf{B_2}+\mathbf{E_2}$
E_2						$A_1+A_2+\mathbf{B_1}+B_2$	$\mathbf{E_1}+E_3$
E_3							$A_1+A_2+E_2$

A detailed scheme, interpreting all the observed infra-red frequencies, is given in Table VI.

TABLE VI

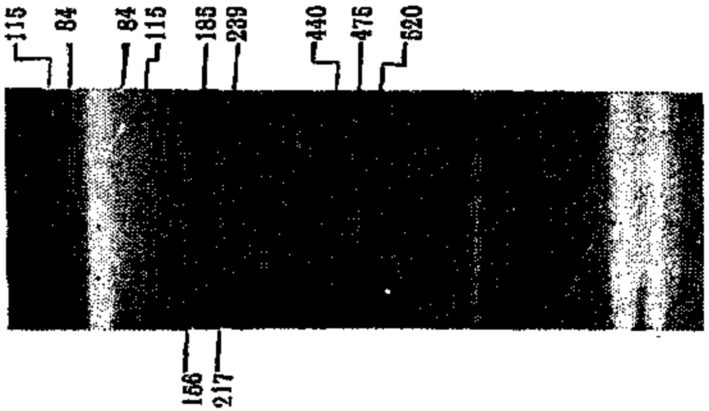
Interpretation of the observed infra-red frequencies

Number	Observed frequency Cm.$^{-1}$	Assignment due to the author	Calculated value only for combinations and overtones Cm.$^{-1}$
1	<77	lattice frequency	..
2	87	"	..
3	104	"	..
4	149	Overtone of < 77	..
5	200	ν_6	..
6	267	$2\ \nu_9$	312
7	400	ν_3	..
8	465	ν_5	..
9	685	$\nu_5 + \nu_2$	682
10	840	$\nu_3 + \nu_{10}$	840
11	932	$\nu_1 + \nu_5$	940
12	1289	$3\ \nu_{10}$	1320

It is needless to add that most of the assignments given by the earlier authors are not in agreement with the selection rules.

7. *Summary*

The complete Raman spectrum of a single crystal of rhombic sulphur has been obtained. Nine frequencies at 84, 115, 156, 185, 217, 239, 440, 475 and 520 cm.$^{-1}$ have been recorded. Of these, the two frequencies at 84 and 115 have been attributed to the lattice and the remaining seven frequencies are taken as the fundamentals appropriate to the S_8 molecule. Out of the eight infra-red absorption maxima recorded by Barnes, the three at 200, 400 and 465 cm.$^{-1}$ are attributed to the molecule. Three others at $<$ 77, 87 and 104 are attributed to the lattice. The other two frequencies observed by Barnes at 149 and 265 and the four infra-red absorption maxima recorded by Taylor and Rideal at 685, 840, 932 and 1289 cm.$^{-1}$ are explained as



Raman Spectrum of Sulphur