RAMAN SPECTRUM AND SPECIFIC HEAT OF SULPHUR.

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1. *Frequencies and Force Constants.*

The equations relating to all the eleven vibrational frequencies that are to be expected of the sulphur molecule when it is regarded as a puckered octagon have been given in a previous paper.* Only seven of these are active in Raman effect and three others are active in infra-red absorption. There is one frequency which is inactive in both Raman effect and infra-red absorption. None of the Raman frequencies are to be expected in the infra-red absorption and *vice versa.* Of the seven frequencies that are to be expected in Raman effect, two come under the total symmetric class (A_1) and should accordingly give rise to two strong and well polarised Raman lines. The Raman spectrum of sulphur[1] does exhibit two strong and well polarised lines at 470 and 216 and these may at once be identified with ν_1 and ν_2 in the notation of the paper already cited. We may now substitute these in the quadratic for λ_1 and λ_2 and obtain approximate values for K_1 and K_2 if we provisionally assume a zero value for K_3. If these are substituted in the expression for ν_7, a value which is in the neighbourhood of 243 is obtained for it. Thus, ν_1, ν_2 and ν_7 are respectively identified with 470, 216 and 243. Using these values, K_1, K_2 and K_3 may be obtained as $K_1 = 2 \cdot 309 \times 10^5$ dynes/cm.; $K_2 = 0 \cdot 903 \times 10^{-11}$ dynes cm./radian; $K_3 = 0 \cdot 0665 \times 10^5$ dynes/cm. K_1, K_2 and K_3 respectively represent the force constants in respect of the primary valence, directed valence and repulsive forces. This set of force constants is used to calculate all the frequencies. The values thus calculated are compared below in Table I with the observed values. Data in respect of infra-red absorption are taken from Barnes.[2] A better agreement may have been obtained by altering the constants slightly but the labour involved will be considerable and it is therefore not attempted.

The dimensions of the molecule are taken from the work of Warren and Burwell.

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* See preceding paper in this *Journal.*

[1] C. S. Venkateswaran, *Proc. Ind. Acad. Sci.,* (A), 1937, **4**, 345.

[2] *Phys. Rev.*, 1932, **39**, 562.

TABLE I. *Normal Frequencies of Sulphur.*

Class	Frequency calculated cm.$^{-1}$	Frequency observed cm.$^{-1}$	
		Infra-red	Raman
A_1	481 197	*f* *f*	470 (P) 216 (P)
B_1	255	267 (w)	*f*
B_2	557	*f*	*f*
E_1	481 181	465 (st) 200 (st)	*f* *f*
E_2	243 456 122	*f* *f* *f*	243 434 (D) 152 (D)
E_3	542 211	*f* *f*	114 (?) 185

In the above Table *f* stands for forbidden, D for a depolarised and P for a well-polarised Raman line. The available polarisation data in respect of Raman lines are included. The intensities of infra-red absorption are indicated in brackets. It may be noted that only two well-polarised Raman lines are observed and of the other five, data available show that two are depolarised. These results are in perfect agreement with what may be expected of the proposed model. All the observed Raman frequencies except the one at 88 have been listed in the above table. Venkateswaran has given good reasons to show that this low frequency is characteristic of the lattice and hence need not be considered here. There is fair agreement between the calculated and observed frequencies in all cases except the one at 542. No line is reported in the neighbourhood of 542 but a weak line has been recorded by Venkateswaran at 114. It is possible that this line at 114 also belongs to the lattice and not to the molecule. In such a case another Raman line in the neighbourhood of 542 is to be expected. Of the various infra-red absorption maxima recorded by Barnes, the two strong ones at 465 and 200 are satisfactorily explained and these are to be regarded as fundamentals. Another weak absorption at 267 is also presumably a fundamental. Other absorption maxima have to be explained as combination tones or overtones.

The relatively small value of K_3 shows that the primary valence and the directed valence forces are the more important ones. This inference is in agreement with the observations of Badger.[3] The value of K_1 obtained in this molecule suggests that the adjacent sulphur atoms are bound to each other by single bonds. Utilising this value, we may calculate the S–S frequency with the help of the relation $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$, where μ is the reduced mass. When expressed in wave-numbers, this comes out as 496 and compares well with 512 observed in disulphides containing this group.[4] If we take the force constant for S = S as twice the value of K_1, *i.e.*, $4 \cdot 618 \times 10^5$ dynes/cm., the corresponding frequency comes out as 702 and agrees well with the vibrational frequency 724 of sulphur vapour obtained from the band spectrum data.

2. *Specific Heat of Sulphur.*

The specific heat at any temperature consists of two parts arising respectively from the rotational and translational motions and the internal vibrations. Following the recent work of Lord, Ahlberg and Andrews,[5] we will assume that the former is represented by $2D\left(\frac{\theta}{T}\right)$, where D is the Debye function and θ is the mean effective characteristic temperature in respect of longitudinal and torsional elastic waves. The value of this is assumed to be 74·5 for sulphur and it corresponds to $\nu = 52$ cm.$^{-1}$. The exact relationship of θ to the observed Raman frequencies in the region of lattice oscillations is not discussed here. The eleven internal vibration frequencies are taken as 152 (2), 185 (2), 200 (2), 216 (1), 243 (2), 267 (1), 434 (2), 465 (2), 470 (1), 542 (2), 557 (1), and an Einstein function is associated with each one of them. The number in parenthesis represents the degree of degeneracy in each case. The sum of all the Einstein functions is the contribution of the latter type to the specific heat. The specific heat thus calculated is compared with the observed specific heat[6] at different temperatures in Table II.

Satisfactory and general agreement between the observed and calculated specific heats is noticed. At temperatures higher than 50° K the observed value is always somewhat larger than the calculated one. This may be due to the fact that the former refers to constant pressure whereas the calculations refer only to constant volume. The recent work of Sirkar and

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[3] *Jour. Chem. Phys.*, 1935, 3, 710.

[4] S. Venkateswaran, *Ind. Jour. Phys.*, 1931, 6, 5.

[5] *Jour. Chem. Phys.*, 1937, 5, 649.

[6] Values are taken from *I.C.T.*, 5 ; Nernst, *Ann. d. Phys.*, 1911, 36, 395.

TABLE II. *Specific Heat of Sulphur.*

Temperature K	$2D\left(\frac{74\cdot5}{T}\right)$	Vibrational contribution	C_v Specific heat calc. (total)	C_p Observed
10	1·96	0	1·96	2·48
20	6·50	0·01	6·51	5·76
30	8·94	0·23	9·17	9·20
40	10·08	1·02	11·10	11·26
50	10·70	2·38	13·08	14·16
60	11·04	4·08	15·12	16·64
70	11·26	5·88	17·14	19·04
80	11·40	7·61	19·01	21·44
90	11·50	9·40	20·90	23·52
100	11·58	11·04	22·62	25·60
150	11·76	17·95	29·71	32·88
200	11·82	22·90	34·72	37·52
250	11·86	26·27	38·13	41·04
300	11·88	28·58	40·46	44·56

Gupta[7] may be referred to in this connection. Their calculations are however incomplete as they have not taken account of all the vibrational frequencies.

3. *Summary.*

Using the expressions derived by us in an earlier paper for the vibrational frequencies of the sulphur, the force constants K_1, K_2 and K_3 referring respectively to primary valence, directed valence and repulsive forces are evaluated. The values obtained are $K_1 = 2\cdot309 \times 10^5$ dynes/cm. ; $K_2 = 0\cdot903 \times 10^{-11}$ dynes cm./radian and $K_3 = 0\cdot06665 \times 10^5$ dynes/cm. The frequencies calculated on the basis of these constants are compared with the observed Raman lines and infra-red absorption maxima and satisfactory agreement obtained.

The specific heat of sulphur is represented as the sum of a Debye function and a number of Einstein functions associated with the various normal frequencies. The calculated values compare favourably with the observed specific heats.

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[7] *Ind. Journ. Phys.*, 1938, **12**, 145.