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R. K. Asundi, Mohd. Jan-Khan and R. Samuel

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By R. K. ASUNDI, MOHD. JAN-KHAN, and R. SAMUEL

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[PLATE 1]

An analysis of the near ultra-violet bands of SO₂, proposed recently* has shown, that the energies of excitation are almost equal in SO and SO₂ and that the frequency of the symmetric valence vibration of SO₂ is about equal to the vibrational frequency of SO not only in the ground states of the two molecules, but also in their respective excited states. These results seem to be of considerable interest, particularly with regard to the theory of valency, since they indicate that the S=O bond is almost identical in both molecules. It seemed necessary, therefore, to investigate the spectra of SeO and SeO₂ in order to see whether such results are fortuitous or whether they are confirmed by the analysis of similar molecules. Such an investigation appeared desirable also, from the point of view that the method of analysis of the spectra of polyatomic molecules has not made so much progress as could be wished for and the bands of formaldehyde† and sulphur dioxide are indeed the only ones, for which a complete vibrational analysis has been offered at the present moment. An extension to polyatomic molecules of the clearer insight into the constitution of diatomic molecules, afforded by band spectroscopy, seems to us essential in the present state of knowledge.

EMISSION SPECTRUM OF SeO

Experimental—The spectrum of SeO has not been described in literature. Various methods of producing bands of SeO, however, suggest themselves. In analogy with SO the best method probably would be one of a discharge through a vacuum tube in running vapour of SeO₂ or with high pressure SeO₂ vapour. SeO₂ being a solid with rather a high melting point (340° C), such a method could not be adopted because of the want of a suitable quartz discharge tube and a suitable furnace. A glass discharge tube, with a quartz window for observation, containing

* Asundi and Samuel, 'Proc. Ind. Acad. Sci.,' vol. 2, p. 30 (1935).

† Dieke and Kistiakowsky, 'Phys. Rev.,' vol. 45, p. 4 (1934); Herzberg, 'Trans. Faraday Soc.,' vol. 27, p. 378 (1931).

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SeO₂ was heated locally by a Bunsen burner, but the spectrum obtained showed only bands due to Se₂. An arc on 110 volts D.C., with a current of 2.5 amps, between carbon or metal electrodes filled with SeO₂, produced again the bands of Se₂ or the lines of Se as did also the arc on 220 volts D.C. with a current of 2 to 5 amps. The substance was then introduced in a solid state and in aqueous solution into the Bunsen flame. The flame of the solid substance gave only Se₂ bands, but the spectrum of the flame of the solution showed an unmistakable progression of bands, different from those of Se₂ between 4500 and 3200 Å. In the hope of exciting more vibrational levels of the emitter of these bands and thus extending the system, the oxy-coal-gas flame giving a higher temperature was used. Under this condition the spectrum showed a further set of bands towards the ultra-violet until about 2400 Å. The bands are all degraded towards longer waves; they are diffuse and in some cases a close double head can be distinguished. The intensity of the bands is not at all high; and increased exposure only resulted in a more pronounced overlap of the bands with the strong continuum of the flame itself. The best plates were obtained, in the blue and near ultra-violet regions, with an exposure of 45 minutes, and in the ultra-violet region, of about two hours, using a Hilger medium quartz spectrograph as the resolving instrument.

That the bands in the blue and near ultra-violet are due to the SeO molecule is fairly certain. They belong decidedly to a diatomic molecule. They appear in the flame of SeO₂ solution and are similar to SO bands. The final plates were measured on the Abbe comparator. On account of the diffuse character of the bands and the accompanying continuum microphotograms on a recording microphotometer were also taken and the band heads measured with the same comparator. The final values of wave-lengths of the band heads were obtained from readings taken on two directly measured plates and three photometer plates. The agreement among various values of the same band heads was not as satisfactory as one would desire. This is due to the inherent diffuseness of the bands and in some cases also to the overlap of OH bands which made it difficult to spot bands lying in that region. The values accepted are therefore correct only to about 1 or 2 Å, *i.e.*, to about 10 or 20 wave-numbers. We have reasons to believe that the weak bands in the further ultra-violet, however, belong rather to the SeO₂ molecule.

Analysis—Table I gives the wave-numbers *in vacuo* of the band heads as obtained from the weighted mean of the five measured values. Figs. 1 and 2, Plate 1, are reproductions of the bands from one of the original

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plates and its microphotometer plate respectively. The starting point for the analysis was the obvious set of bands beginning from the band at $30,433 \text{ cm}^{-1}$ towards longer waves. These bands fall into a progression with vibrational differences, 873, 866, 849, 835, 848, and 823 cm^{-1} . These differences are slightly irregular, as can be seen from Table II, which displays the analysis of the bands. The second progression from $30,941 \text{ cm}^{-1}$ also fits into the scheme fairly well.

TABLE I—LIST OF OBSERVED BANDS

ν vac. cm^{-1} SeO bands	ν vac. cm^{-1} Further ultra-violet bands
25341	33948
26164	35765
27012	36777
27847	37252
27909	37681
28694	38228
28760	38575
(29223)	39075
29274	39498
29560	39972
30076	
30139	
30433	
30941	

The first progression is evidently $v' = 0$ and therefore the second is $v' = 1$. But it is doubtful whether the band at $30,433 \text{ cm}^{-1}$ is the (0, 0) band. Most probably it is not; because the molecule SeO should resemble SO, the intensity distribution here should be characterized by a wide Condon parabola whose apex would certainly not be at (0, 0) but would lie at a band with a higher value of v'' . From this point of view we think that in Table II, x will have a value of 3. This would place the origin at about $33,102$ and $33,167 \text{ cm}^{-1}$ respectively for the two heads and the first vibrational difference of the final state will be about 910 cm^{-1} . The $v' = 0$ progression in Table II as it is, can be expressed by the following formula:

$$\nu = 30433 \left. \vphantom{\nu} \right\} - (882v'' - 6v''^2).$$

The existence of apparent double heads in this band system which is probably due to a transition ${}^3\Sigma \rightarrow {}^3\Sigma$ in analogy with O_2 and SO, is to be regarded as accidental. The head at the shorter wave-length is the weaker one, and there is a difference of roughly 65 cm^{-1} between the two

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TABLE II

$\begin{array}{c} \cancel{v''} \\ v' \end{array}$	x	x + 1	x + 2	x + 3	x + 4	x + 5	x + 6
0	— 30433 (508)	— 29560 (873)	28760 28694 (866)	(851) 27909 (847) 27847	— 27012 (835)	— 26164 (848)	— 25341 (823)
1	— 30941	(516) 30139 (865)	(514) 29274 (853)	29223 ?			

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heads. This distance appears to be the average distance between the origin and the head of the individual bands, the apparent strong head being due to the unresolved lines of the three P branches which should be strong and the two P-form Q branches and the two R-form Q branches, which all should be weak and which start roughly near about the origin.

The vibrational function of the initial state cannot be evaluated for want of more progressions, but the first frequency difference is $\omega' = 513 \text{ cm}^{-1}$.

The set of weak bands in the further ultra-violet does not seem to belong to this system at all. It was by no means possible to arrange them as an extension of the present system. Comparison of these bands with the absorption bands of SeO_2 shows that they are really due to the SeO_2 molecule, as can be seen by comparing Table I with Table III. They are identical inside the experimental error, with the bands due to a few transitions arising mostly from the vibrationless ground state of the molecule SeO_2 .

ENERGY OF DISSOCIATION

Linear extrapolation of the vibrational levels gives a value of 4.17 volts for the energy of dissociation (D) of the ground level of SeO. This value agrees very well with what one would expect from the dissociation energies of O_2 and SO.* It is a general feature throughout the periodic system that the dissociation energy runs parallel to the strength of the nuclear fields, regardless of the polarity of the molecule.† In a series of oxides, in which the field of the O atom remains unchanged throughout, D should therefore follow roughly the ionization potential of the other atom, and this is true in each individual group of the periodic system, as may be seen from the following few examples.

Since for SO and SeO we have to use the value obtained from linear extrapolation, we have given in Table III besides the actual value of $D(\text{O}_2) = 5.09$ directly deduced from the convergence point of the

TABLE III

	CO	SiO	GeO
D =	10.45	7.8	7.3 volts
	O_2	SO	SeO
D =	6.56 } 5.09 }	5.1	4.17 volts

Schumann-Runge bands,* also the value 6.56 which follows from linear

* Herzberg, 'Z. phys. Chem.,' B, vol. 10, p. 189 (1930); Frerichs, 'Phys. Rev.,' vol. 36, p. 398 (1930); Martin, 'Phys. Rev.,' vol. 41, p. 167 (1932).

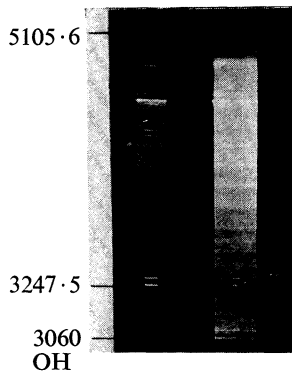


FIG. 1.

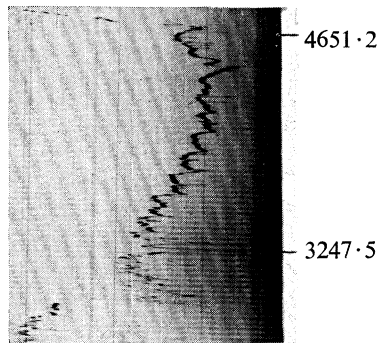


FIG. 2.

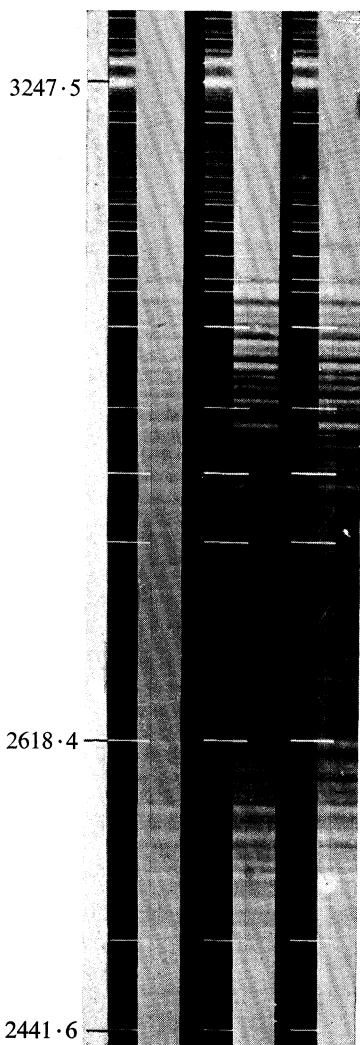


FIG. 3.

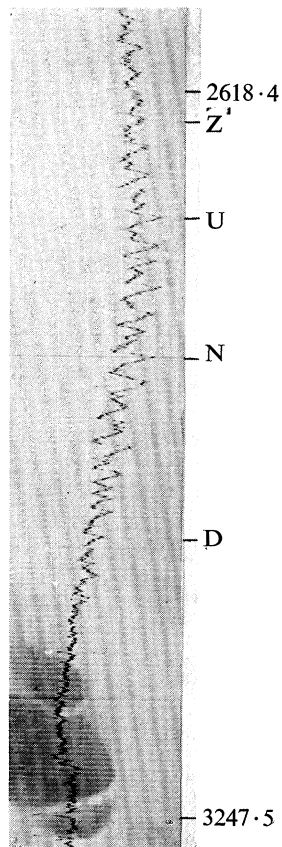


FIG. 4.

extrapolation. Furthermore, it has been shown* that if we consider diatomic molecules built up of atoms of similar groups of the periodic system, so that the sum of the numbers expressing the periods of the two atoms remains the same, the dissociation energies of such similar molecules remains very often rather constant. This is clear from Table IV, which refers to their respective ground states.

TABLE IV

	CS	GeS	CP	PO	Br ₂
D =	7.75	5.7	6.9	6.47	2.0 volts
	SiO	SnO	SiN	NS	ICI
D =	7.8	5.8	6.2	5.93	2.1 volts

According to this, the dissociation of SeO should be about the same as that of S₂, which on considerations of predissociation and linear extrapolation has been estimated as 4.45 volts.† In reality even this value is slightly too high. The direct observation of the point of convergence yields naturally a more exact value; this has been observed in the absorption spectrum of S₂ vapour by Rosen‡ as $40,000 \pm 1000 \text{ cm}^{-1} = 4.94 \pm 0.12$ volts. If we subtract from this, the energy of excitation of the ¹D term, which is 1.14 volts,§ we obtain 3.8 ± 0.12 volts as the energy of dissociation of S₂ in the normal state. The extrapolated value for SeO is 4.17 volts, in good agreement with the above rule.

The fact that the extrapolated value of SeO agrees with that value of S₂, which is taken from the convergence limit, is an indication of the absence in the SeO bands of such perturbations as destroy the application of the linear extrapolation for the calculation of the energy of dissociation of S₂. This is in agreement with the view of Heil,|| according to whom the repulsive curve arising from the combination of two unexcited atoms of the sixth group intersects the potential curve of the excited state of the molecule at lower vibrational levels and finally not at all, with increasing atomic numbers. The case of SeO seems already to be near to that of Se₂, where the repulsive curve does not intersect at all.

ABSORPTION SPECTRUM OF SeO₂

Experimental—The absorption spectrum of SeO₂ was obtained in the usual way, the substance being introduced in an evacuated silica tube,

* Lessheim and Samuel, 'Proc. Ind. Acad. Sci.', vol. 1, p. 623 (1935), Sect. x ff.

† Christy and Naude, 'Phys. Rev.', vol. 37, p. 903 (1931).

‡ 'Z. Physik,' vol. 43, p. 69 (1927).

§ Ruedy, 'Phys. Rev.', vol. 43, p. 1045 (1933).

|| 'Z. Physik,' vol. 74, p. 18 (1932).

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heated by an electric furnace to various temperatures. As source of light the continuous spectrum of hydrogen was used, and as resolving instrument a Hilger medium quartz spectrograph; copper arc lines were utilized as standards. The plates obtained in this way were again run through the recording microphotometer and these microphotograms measured directly. Figs. 3 and 4, Plate 1, are reproductions of an original plate and a microphotogram.

The wave-lengths ultimately adopted are the weighted means of four values obtained by direct measurement of spectrograms and of two of the microphotograms. Of the subsidiary maxima observed in the microphotograms, only such as are obtained on both the plates and which do not differ in wave-length by more than 0.2 Å have been accepted. The wave-lengths obtained from each of these six measurements did not differ by more than 0.5 Å and therefore the accuracy of the accepted mean wave-length is believed to be not less than 0.2 Å or 2 to 6 cm^{-1} in the region covered by the bands. A few of the bands, however, on the extreme long and short wave sides respectively, of the system could be measured on some of the plates taken at higher temperatures only. The accuracy obtained for such bands only is not greater than 1 Å in each case, *i.e.*, 10 to 15 cm^{-1} . Table V gives the wave-lengths in air, wave-numbers *in vacuo*, and their classification with the observed minus calculated values, the latter being based on the mean values of the spacings of the vibrational levels (Table VII).

TABLE V—LIST OF SeO_2 BANDS

Bands	λ Å (in air)	ν cm^{-1} (<i>in vacuo</i>)	Classification	O - C
<i>a</i>	3158.1	31655	(010)'' → (000)'	-4
<i>b</i>	3116.0	32083	(020)'' → (020)'	-1
<i>b</i> 1	3107.5	32171	(001)'' → (001)'	+10
<i>c</i>	3092.0	32332	{ (010)'' → (010)' (020)'' → (002)'	+10 -10
<i>d</i>	3070.4	32560	(000)'' → (000)'	0
<i>e</i>	3044.4	32838	{ (001)'' → (011)' (011)'' → (003)'	+14 -4
<i>f</i>	3032.8	32963*	(010)'' → (020)'	-11
A 1	3008.9	33225*	(000)'' → (010)'	+2
A 2	3007.8	33237	(010)'' → (002)'	+5
B	2986.5	33474*	(001)'' → (021)'	-2
C 1	2972.8	33629*	(010)'' → (030)'	+8
C 2	2963.6	33733*	(001)'' → (003)'	-2
D	2950.9	33878*	(000)'' → (020)'	+3
E	2928.6	34136	{ (000)'' → (002)' (001)'' → (031)'	+3 +13
F 1	2917.2	34269*	(010)'' → (040)'	+9

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TABLE V—(continued)

Bands	λ A (in air)	ν cm ⁻¹ (in vacuo)	Classification	O - C
F 2	2915.7	34287*	(020)'' → (032)'	-17
G	2906.6	34394	{ (001)'' → (013)' (011)'' → (005)'	-4 -2
H 1	2895.6	34525*	(000)'' → (030)'	+3
H 2	2894.3	34541*	(010)'' → (022)'	-6
I 1	2884.5	34658	(020)'' → (060)'	+6
I 2	2872.7	34800	{ (000)'' → (012)' (010)'' → (004)'	+4 -2
K	2860.8	34945	(020)'' → (042)'	+2
L 1	2851.4	35060*	(001)'' → (023)'	+10
L 2	2843.4	35159	(000)'' → (040)'	-2
L 3	2841.3	35185*	(010)'' → (032)'	-9
L 4	2839.1	35212	(020)'' → (024)'	-15
L 5	2831.4	35308	{ (001)'' → (005)' (020)'' → (070)'	+11 -3
M	2819.8	35453	{ (000)'' → (022)' (020)'' → (006)' (010)'' → (014)'	+5 -11 -12
N	2800.6	35696	{ (000)'' → (004)' (001)'' → (033)'	-7 -3
O 1	2790.7	35823	{ (000)'' → (050)' (010)'' → (042)'	+13 -10
O 2	2788.3	35854*	(020)'' → (034)'	-20
O 3	2783.0	35922	(011)'' → (007)'	-4
O 4	2781.9	35936	(020)'' → (080)'	-12
O 5	2780.4	35955	(001)'' → (015)'	-5
P 1	2772.7	36053	(001)'' → (061)'	+9
P 2	2769.5	36097*	(000)'' → (032)'	-2
P 3	2768.0	36117	{ (010)'' → (024)' (020)'' → (016)'	0 -10
Q 1	2750.3	36349	{ (001)'' → (043)' (010)'' → (006)'	+13 -5
Q 2	2748.6	36371*	(000)'' → (014)'	+5
R 1	2739.6	36491	(010)'' → (052)'	+9
R 2	2738.3	36508*	(020)'' → (044)'	-5
S	2731.1	36606*	(001)'' → (025)'	-6
T 1	2721.0	36740*	(000)'' → (042)'	+6
T 2	2719.4	36762*	(010)'' → (034)'	-2
T 3	2713.9	36836	(001)'' → (007)'	+9
U 1	2700.8	37015	{ (000)'' → (024)' (020)'' → (008)'	-3 +12
U 2	2700.2	37023	(010)'' → (016)'	+6
V 1	2694.0	37109	{ (000)'' → (070)' (010)'' → (062)'	+7 +6
V 2	2690.0	37164*	(020)'' → (054)'	+2
W	2683.3	37256	{ (000)'' → (006)' (001)'' → (035)'	+1 -3

TABLE V—(continued)

Bands	γ A (in air)	ν cm ⁻¹ (<i>in vacuo</i>)	Classification	O — C
X 1	2673·8	37389*	(000)'' → (052)'	+6
X 2	2671·1	37427	(020)'' → (036)'	+1
Y 1	2665·8	37501*	(001)'' → (017)'	+11
Y 2	2653·7	37672	{ (000)'' → (034)' (010)'' → (026)' (020)'' → (018)'	+7 +3 +6
Y 3	2649·6	37730	(000)'' → (080)'	-9
Y 4	2644·7	37800*	(020)'' → (064)'	+5
Z 1	2638·4	37890	(010)'' → (008)'	-3
Z 2	2636·7	37901*	(001)'' → (045)'	+3
Z 3	2635·9	37926	(000)'' → (016)'	+8
A' 1	2629·3	38022*	(000)'' → (062)'	+6
A' 2	2625·9	38071	(020)'' → (046)'	+6
A' 3	2620·4	38151	(001)'' → (027)'	+9
B' 1	2609·2	38314	{ (000)'' → (044)' (010)'' → (036)'	+10 -2
B' 2	2600·4	38444*	(020)'' → (074)'	-10
C' 1	2593·3	38549*	(001)'' → (055)'	+2
C' 2	2592·9	38555	{ (000)'' → (026)' (010)'' → (018)'	-15 -1
D' 1	2584·5	38681*	(000)'' → (072)'	+6
D' 2	2583·5	38697	(020)'' → (056)'	-17
D' 3	2577·6	38784	{ (000)'' → (008)' (001)'' → (037)'	-10 -5
E' 1	2569·1	38912*	(001)'' → (083)'	-2
E' 2	2565·7	38964	{ (010)'' → (046)' (000)'' → (054)' (020)'' → (038)'	+9 +11 -1
E' 3	2557·0	39097*	(020)'' → (084)'	+6
F' 1	2549·6	39210	{ (000)'' → (036)' (010)'' → (028)'	-7 +2
F' 2	2542·6	39318*	(000)'' → (082)'	+6
F' 3	2536·4	39414*	(001)'' → (047)'	-14
F' 4	2533·9	39453*	(000)'' → (018)'	-4
G'	2524·6	39598	{ (010)'' → (056)' (000)'' → (064)' (020)'' → (048)'	-6 +12 -6
H'	2508·5	39852	{ (000)'' → (046)' (001)'' → (075)' (010)'' → (038)'	-4 +13 -3
I' 1	2495·3	40063*	(001)'' → (057)'	-14
I' 2	2493·2	40097*	(000)'' → (028)'	-12
K'	2470·1	40472	(001)'' → (085)'	-4
L'	2459·7	40643	(020)'' → (086)'	0
M'	2455·3	40716	(001)'' → (067)'	+6
O'	2430·4	41133	(000)'' → (066)'	-5
P'	2417·0	41361	(001)'' → (077)'	-8

ANALYSIS

The analysis of a band system due to a triatomic molecule is necessarily difficult. For a diatomic molecule, on account of a single vibrational frequency being involved in either state, the disposition of the bands in the spectrogram is rather regular, so that by a mere glance at the plate one can often pick out sequences or progressions with a great deal of certainty. Even here for molecules for which the intensity distribution of the band system arises out of a transition involving a considerable change in inter-nuclear distance and frequency of vibration, such a regularity of appearance is absent, thus rendering the analysis rather difficult. This difficulty is further enhanced in a triatomic molecule, where the same type of intensity distribution may occur for one or all of the frequencies concerned. Therefore, an attempt to seek a regularity in appearance is often misleading. On account of the large number of bands and on account of constant differences which may arise in altogether different ways, *e.g.*, from a difference between two entirely different modes of vibrations of the same electronic state, it is nearly always possible to find a few bands with a constant difference of wave-numbers among the large number of bands observed. Such a frequency difference is therefore no definite indication of the magnitude of the difference of frequencies of the same mode of vibration in the initial and final state.

Another, and to our mind, preferable method of attack would be to select the $(0, 0, 0)'' \rightarrow (0, 0, 0)'$ transition first and then try to find an analysis which obtains for the ground state such vibrational frequencies as are known already from considerations of Raman and infra-red spectra. An approximate selection of the vibrationless transition is rendered possible from two considerations. First, a comparison of the relative intensities of the $(0, 0, 0)'' \rightarrow (0, 0, 0)'$ band and another one, involving a higher vibrational level of the ground state, should show that at higher temperatures the latter gains in relative intensity since then the number of molecules is increased in the excited vibrational levels of the ground state at the expense of the population in the $(0, 0, 0)''$ level. Secondly, the $(0, 0, 0)'' \rightarrow (0, 0, 0)'$ transition may be singled out approximately by considerations of the energy of excitation of the molecule. We know from a good deal of experimental evidence of the spectra of diatomic molecules as well as the absorption spectra of polyatomic molecules in the vapour or liquid state and in solution, that in a series of homologous molecules the energies of excitation together with the bond energies decrease with increasing mass of the molecule, *e.g.*, in SeO_2 the origin of the band system is expected to be shifted slightly towards longer wave-

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lengths than for SO_2 . The latter being at 3001.9 \AA the origin of the SeO_2 bands might be expected to be slightly higher than this. On the other hand, assuming a similar relation for SeO and SeO_2 as has been found for SO and SO_2 , we may expect the origin of the SeO_2 band system to be nearly at the same wave-length as that of SeO . A slight shift towards longer wave-length is, however, to be expected on account of the additional repulsive force between the two oxygen atoms, which tend slightly to weaken the bond energies. This force, however, should be considerably less than in SO_2 , because of the increased internuclear distances due to the increased radius of the central atom. From the above figures of the origin of the SeO bands we obtain, therefore, a wave-length of about 3020 \AA as the lower limit.

The vibrational frequencies of the ground state of SeO_2 are not known either from the infra-red or the Raman spectra. A comparison of the known frequencies of SO_2 with those of the sulphates from Raman effect shows that the values from the sulphates give only a lower limit. In the same way, the known frequencies of the selenates give a lower limit for those of selenium dioxide. On the other hand, the frequencies of SO_2 will give us an upper limit on account of the increased mass of SeO_2 . The deforming, the symmetric, and antisymmetric valence vibrations of SO_2 have the values $\omega_1 = 525$, $\omega_2 = 1150$, and $\omega_3 = 1360 \text{ cm}^{-1}$ respectively. The Raman frequencies of the selenates* are 875 , 835 , 415 , and 342 cm^{-1} and the corresponding figures of SeO_2 should be between these two sets.

With this preliminary knowledge about the approximate position of the origin and the approximate magnitude of the three fundamental frequencies, an attempt was made to analyse the bands observed in SeO_2 . After several unsuccessful attempts with various possible values for the $(0, 0, 0)'' \rightarrow (0, 0, 0)'$ band, it was ultimately found that starting from the band at $32,560 \text{ cm}^{-1}$ as the origin, it was possible to assign the bands observed to transitions connected with the frequencies ω'_2 , ω''_2 , ω'_3 , and ω''_3 .

The analysis is displayed in Tables VA to VG. It will be seen that for the same vibrational spacings from different transitions different values are obtained which slightly disagree among themselves. This, we believe, is due to the fact that we do not measure the origin of the bands nor even their heads but the point of maximum intensity in each band, and the distance of this point from the true origin of the band cannot be supposed to remain constant in the different transitions in different modes of vibration. Such discrepancies are quite well known even in diatomic

* Ganesan, 'Proc. Ind. Acad. Sci.', vol. 1, p. 156 (1934).

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TABLE VA—BANDS DUE TO THE SIMPLE TRANSITIONS

		$(0, v_2, 0)'' \rightarrow (0, v_2 0)'$			
$(0v0)''$	$(0v0)''$	0	1	2	
0	0	32560 (665)	(905) 31655 (677)	—	
1	1	33225* (653)	(893) 32332 (631)	—	
2	2	33878 (647)	(905) 32963* (666)	(880)	32083
3	3	34525* (634)	(896) 33629* (640)	—	
4	4	35159 (664)	(890) 34269*	—	
5	5	35823	—	—	
6	6	—	—	34658 (650)	
7	7	37109 (621)	—	35308 (628)	
8	8	37730	—	35936*	

TABLE VB—BANDS DUE TO THE SIMPLE TRANSITIONS

		$(0, 0, v_3)'' \rightarrow (0, 0, v_3)'$	
$(00v)''$	$(00v)''$	0	1
0	0	32560	—
1	1	—	32171
2	2	34136	—
3	3	—	33733*
4	4	35696	—
5	5	—	35308
6	6	37256	—
7	7	—	36836
8	8	38784	—

TABLE VC—BANDS DUE TO THE CROSS TRANSITIONS

		$(0, v_2, 0)'' \rightarrow (0, 0, v_3)'$		
$(00v)''$	$(0v0)''$	1	2	
0	0	31655 (1582)	—	
2	2	33237 (1563)	(905)	32332
4	4	34800 (1549)	—	
6	6	36349 (1541)	(896)	35453 (1562)
8	8	37890	(875)	37015

TABLE VD—BANDS DUE TO COMPOSITE TRANSITIONS FROM GROUND STATE $(0, 0, 0)''$

		$(0, 0, 0)'' \rightarrow (0, v_2, v_3)'$			
$v_2 \backslash v_3$		2	4	6	8
0		34136 (664)	35696 (675)	37256 (670)	38784 (669)
1		34800 (653)	36371* (644)	37926 (629)	39453* (644)
2		35453 (644)	37015 (657)	38555 (655)	40097
3		36097* (643)	37672 (642)	39210 (642)	—
4		36740* (649)	38314 (650)	39852	—
5		37389* (633)	38964 (634)	—	—
6		38022* (659)	39598	41133	—
7		38681* (637)	—	—	—
8		39318*	—	—	—

TABLE VE—BANDS DUE TO COMPOSITE TRANSITIONS FROM $(0, 1, 0)''$

		$(0, 1, 0)'' \rightarrow (0, v_2, v_3)'$			
$v_2 \backslash v_3$		2	4	6	8
0		33237	34800 (653)	36349 (674)	37890 (665)
1		—	35453 (664)	37023 (649)	38555 (655)
2		34541* (644)	36117 (645)	37672 (642)	39210 (642)
3		35185 (638)	36762*	38314 (650)	39852
4		35823 (668)	—	38964 (634)	—
5		36491 (624)	—	39598	—
6		37115	—	—	—

Spectra of SeO and SeO₂

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TABLE VF—BANDS DUE TO COMPOSITE TRANSITIONS FROM (0, 2, 0)''

(0, 2, 0)'' → (0, v_2 , v_3)'				
$v_2' \backslash v_3'$	2	4	6	8
0	32332	—	35453 (664)	37015 (657)
1	—	—	36117	37672
2	—	35212 (642)	—	—
3	34287* (658)	35854* (654)	37427 (644)	38964 (634)
4	34945	36508* (656)	38071 (626)	39598
5	—	37164* (636)	38697	—
6	—	37800* (644)	—	—
7	—	38444* (653)	—	—
8	—	39097*	40643	—

TABLE VG—BANDS DUE TO COMPOSITE TRANSITIONS FROM (0, 0, 1)''

(0, 0, 1)'' → (0, v_2 , v_3)'				
$v_2' \backslash v_3'$	1	3	5	7
0	32171 (667)	33733 (661)	35308 (647)	36836 (665)
1	32838 (636)	34394 (666)	35955 (651)	37501* (650)
2	32474* (662)	35060* (636)	36606* (650)	38151 (633)
3	34136	36696 (653)	37256 (645)	38784 (630)
4	—	36349	37901* (648)	39414* (649)
5	—	—	38549*	40063* (653)
6	36053	—	—	40716 (645)
7	—	—	39852 (620)	41361
8	—	38912*	40472	—

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molecules, and we have to expect them to a greater degree here. The increased accuracy of measurement brings out this discrepancy, which by its existence we would rather take as an indication of the essential correctness and not otherwise of the analysis.

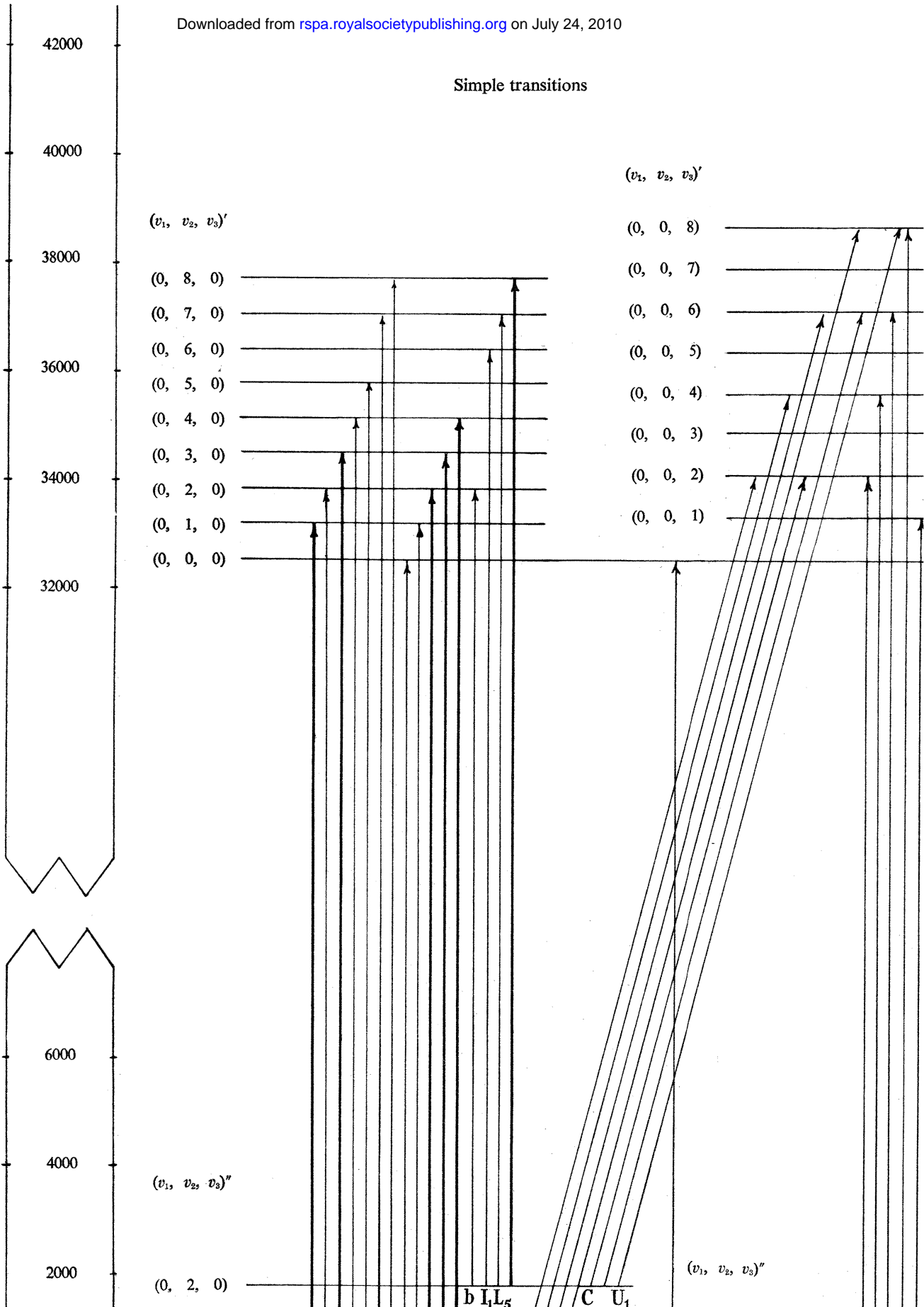
This choice of the origin is corroborated by intensity measurements at different temperatures. That the population of the higher vibrational levels will increase with higher temperature as mentioned above, is shown in Table VI which gives the relative intensities of a number of bands together with their classification, which follows from this choice of the origin of the band system.

TABLE VI—RELATIVE INTENSITIES OF SOME BANDS AT DIFFERENT TEMPERATURES

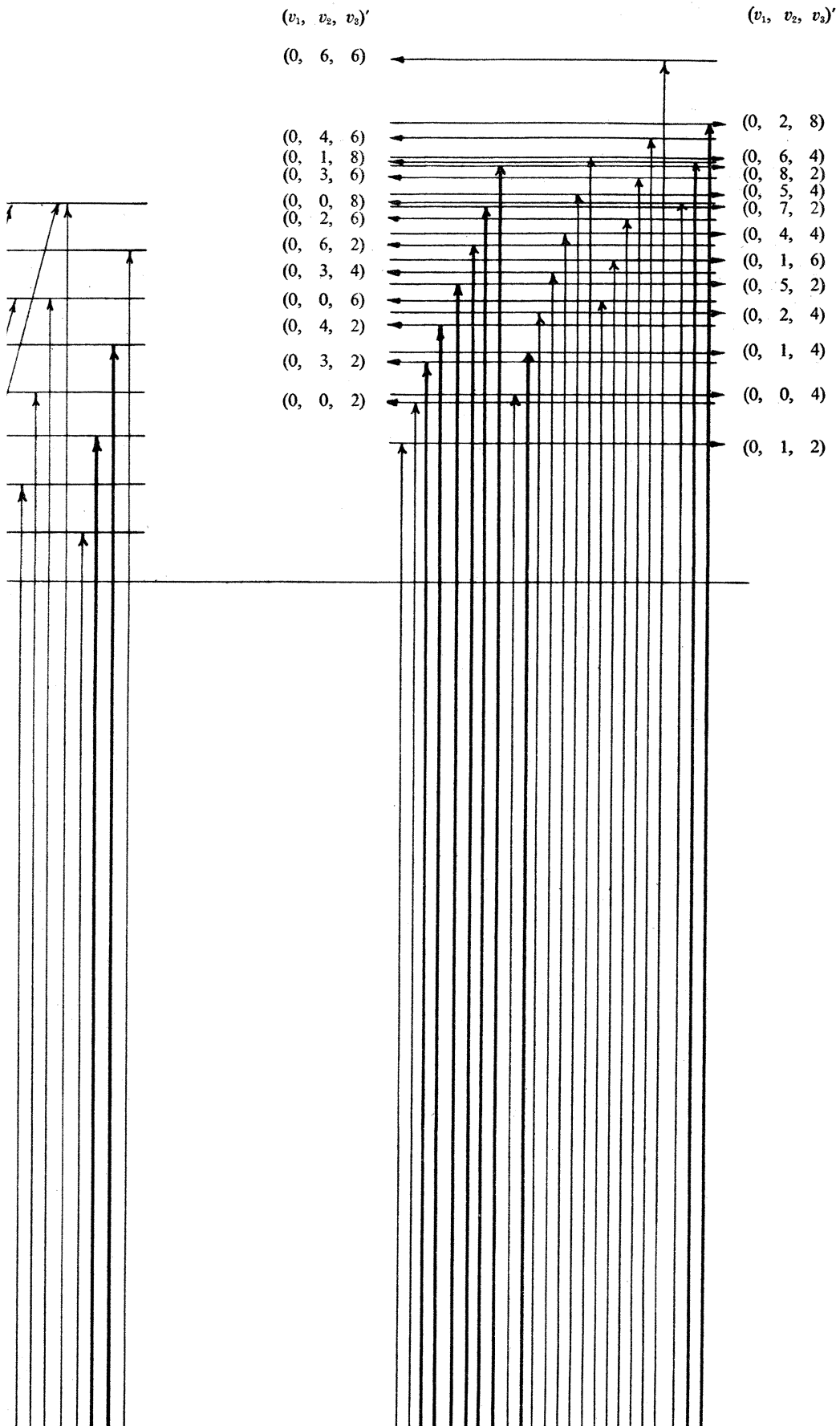
Bands	Relative intensity at 290° C, 2 mm pressure	360° C, 6 mm pressure
$\frac{(0, 0, 0)'' \rightarrow (0, 0, 0)'}{(0, 0, 1)'' \rightarrow (0, 0, 7)'}$ }	1: 7·1	1: 20·0
$\frac{(0, 0, 0)'' \rightarrow (0, 0, 0)'}{(0, 0, 1)'' \rightarrow (0, 6, 1)'}$ }	1: 6·9	1: 20·3
$\frac{(0, 0, 0)'' \rightarrow (0, 0, 0)'}{(0, 1, 0)'' \rightarrow (0, 1, 6)'}$ }	1: 7·2	1: 20·9
$\frac{(0, 0, 0)'' \rightarrow (0, 0, 0)'}{(0, 2, 0)'' \rightarrow (0, 6, 0)'}$ }	1: 5·9	1: 18·3

Fig. 5 is a graphical representation of the simple transitions and one typical set of composite transitions, involved in the production of the bands of SeO_2 whose classification is also shown in Table V. As in SO_2 , we again obtain only two frequencies, *i.e.*, ω_2 and ω_3 in the ground state and the same two frequencies in the excited state. For each of these frequencies in the excited state, eight vibrational levels and in the normal state two and one respectively of each mode of vibration are obtained. Table VII gives the mean spacings of these levels as obtained by the analysis.

The spacings in the excited state are not regular, but we cannot definitely say that they are irregular. Some of the bands can be classified in more than one way, as shown in Table V, within the limits of accuracy of measurement and considering the fact that, far from measuring the origin of each band, we do not measure even its head but only the point of maximum intensity, which is affected by the overlap of neighbouring bands, we can generally say that the progressions are regular and there is no indication of pronounced perturbations.



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2000

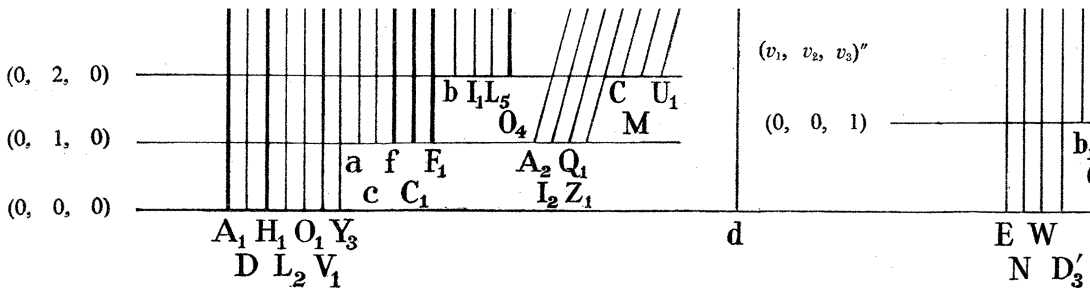
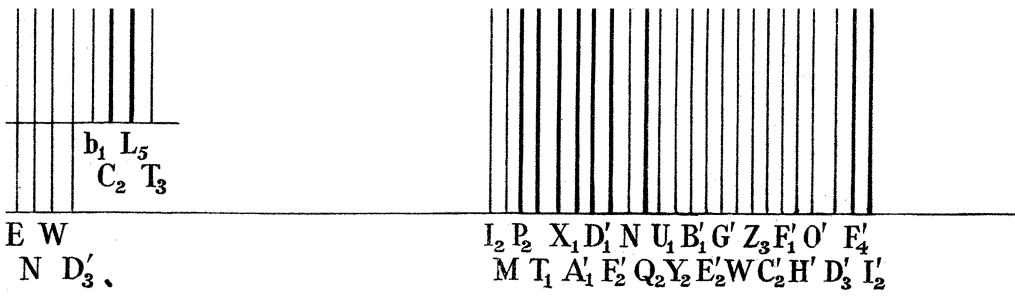


FIG. 5.



(Facing p. 42)

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INTENSITY DISTRIBUTION

There are a few points of interest regarding the intensity distribution in the band system. Of course, it is not possible to come to very definite conclusions because in the first place the intensities estimated are relative and are deduced directly from the heights of the peaks in the microphotograms. Secondly, in estimating this intensity the influence of

TABLE VII—SPACINGS OF VIBRATIONAL LEVELS

Mode of vibration	Level	cm ⁻¹	Difference
ω''_2	{ 0	0	—
	{ 1	901	901
	{ 2	1791	890
ω'_2	{ 0	0	—
	{ 1	663	663
	{ 2	1312	649
	{ 3	1959	647
	{ 4	2602	643
	{ 5	3351	649
	{ 6	3987	636
	{ 7	4637	650
{ 8	5272	635	
ω''_3	{ 0	0	—
	{ 1	1189	1189
ω'_3	{ 0	0	—
	{ 1	790	790
	{ 2	1573	783
	{ 3	2364	791
	{ 4	3143	779
	{ 5	3926	783
	{ 6	4695	769
	{ 7	5456	761
{ 8	6234	778	

superposed bands cannot be eliminated. Thirdly, we take only the point of maximum intensity of each band and not its integrated value. Therefore considerations of intensity distribution which are offered here are only qualitative, but it is believed that even such a qualitative description of the intensity distribution will give us some idea as to the relative positions of the three dimensional potential troughs of the two electronic states.

In fig. 5 we have marked by thick lines those bands, which have got a

high intensity and possess at the same time only a single classification, which excludes to a certain extent the possibility of superposition. Also in Tables V to VG, such bands are marked by an asterisk. It will be seen that in the simple transitions $\omega''_2 \rightarrow \omega'_2$ the strongest bands are those from $v''_2 = 0$ to $v'_2 = 1, 2$, and 3, and from $v''_2 = 1$ to $v'_2 = 2, 3, 4$. In the transitions of $\omega''_3 \rightarrow \omega'_3$ no strong bands occur which have only one classification; but the general trend is that the stronger bands have a slightly larger Δv value. The transitions of $\omega''_2 \rightarrow \omega'_3$ are definitely weak. Among the composite transitions, those which arise from the unexcited vibrational state $(0, 0, 0)''$ (Table VD) are strongest in combination with $(0, v_2, 2)'$ and weaker in combination with $(0, v_2, 4)'$. The composite bands which arise from $(0, 1, 0)''$ are also weak (Table VE). Among them the transitions $(0, 1, 0)'' \rightarrow (0, v_2, 2)'$ are the most favoured, while $(0, 1, 0)'' \rightarrow (0, v_2, 6)'$, and $(0, v_2, 8)'$ are rather fragmentary. Among the transitions from $(0, 2, 0)''$ (Table VF), however, those which go to $(0, v_2, 4)'$ are stronger than those to $(0, v_2, 2)'$, or $(0, v_2, 6)'$, or $(0, v_2, 8)'$. On the other hand, in transitions from $(0, 0, 1)''$ (Table VG) the intensity appears to decrease in the following order:— $(0, 0, 1)'' \rightarrow (0, v_2, 5)' > (0, 0, 1)'' \rightarrow (0, v_2, 7)' > (0, 0, 1)'' \rightarrow (0, v_2, 3)'$. The transition $(0, 0, 1)'' \rightarrow (0, v_2, 1)'$ is definitely weak.

These peculiarities indicate that, if we consider the cross-section in such a plane of the three dimensional potential troughs, as gives us the Franck-Condon curves with respect to ω''_2 and ω'_2 , we can say that here we have the normal behaviour as in a diatomic molecule for which $r'_0 > r''_0$ and $\omega'_0 < \omega''_0$; particularly the turning points of the vibrational level $v''_2 = 0$ will be rather perpendicularly below those of $v'_2 = 2$ (the combinations with 1 and 3 occurring also) and those of $v''_2 = 1$ perpendicularly below those of $v'_2 = 3$ (the combinations with 2 and 4 occurring also). Similar considerations indicate that in a plane representing mainly a cross-section with respect to ω_3 we find again $r'_0 > r''_0$ and $\omega'_0 < \omega''_0$, but the difference $r'_0 - r''_0$ is enhanced as compared to that in the ω_2 plane. This view explains also the above peculiarities of intensity distribution among the composite transitions.

SELECTION RULES

Recently Herzberg and Teller* have deduced selection rules for transitions between the vibrational levels of the electronic terms of polyatomic molecules from considerations of a generalized Franck-Condon principle and of the symmetry properties of a molecule. According to

* 'Z. phys. Chem.,' B, vol. 21, p. 410 (1933).

this theory, transitions involving an antisymmetric frequency should occur, if at all, with low intensity and only if $\Delta v_{(\text{antisym})}$ is an even number. This rule is rigorously valid so long as the change of internuclear distance between normal and excited state is not too big; in case $r'_0 - r''_0$ is considerable also odd changes of $v_{(\text{antisym})}$ may occur, the corresponding transitions leading with low intensity either to a forbidden electronic level or to one which involves a forbidden component of electric moment. The spectrum of selenium dioxide shows one peculiarity which is not accounted for by Herzberg and Teller's theory, *i.e.*, that the deforming vibration ω_1 does not occur at all. The deforming vibration is also a symmetric one and should therefore appear with greater intensity than the antisymmetric valence vibration ω_3 . Naturally we have tried to find progressions with distances of about 300 cm^{-1} to 400 cm^{-1} , which we believe will be the order of magnitude of the deforming vibrations. But an analysis on such a basis, appears to be impossible. In this respect the band system of SeO₂ resembles that of SO₂ completely, and therefore it seems likely that the complete absence of the deforming vibration rather indicates a principal deficiency of the theory. With respect to the selection rule for the antisymmetric mode of vibration ω_3 , however, the result of the analysis is an even better confirmation of Herzberg and Teller's theory than that of SO₂ bands. In sulphur dioxide the Δv_3 selection rule for the antisymmetric mode of vibration was not rigorously valid since a few isolated transitions occurred involving an odd change in v_3 . A glance at fig. 5 shows, however, that here, in the case of SeO₂, the said selection rule is valid in its rigorous form. Thus, among the simple transitions there occur only those between $v''_3 = 0$ to $v'_3 = 0, 2, 4, 6,$ and 8 , and from $v''_3 = 1$ to $v'_3 = 1, 3, 5,$ and 7 . Among the composite bands we find transitions from $(0, v_2, 0)''$ to $(0, v_2, v_3)'$ in which v''_2 and v'_2 have various odd and even values, v'_3 , however, having only the even values $0, 2, 4, 6,$ and 8 . Again transitions occur from $(0, 0, 1)''$ to the $(0, v_2, v_3)'$ levels, in which again v'_2 possess odd and even values, v'_3 , however, is always odd. Whenever v''_3 has an even value, v'_3 has only even values, the odd ones being absent and whenever v''_3 is odd, v'_3 is odd too, the even values being absent. This is indeed a surprisingly good agreement with the theoretical predictions of Herzberg and Teller, and confirms our view that the present method of attack is indeed better suited for an analysis of the complicated band systems of polyatomic molecules.

CHARACTER OF THE BONDS AND BOND ENERGY

As is well known, there exist two different conceptions as regards the theory of valency.* It is possible to describe covalent linkage as due to an effect of single, non-localized electrons, and such a description assumes that the bonding effect due to the degeneracy of the nuclear fields predominates compared with that due to the degeneracy owing to the equality of the electrons. The other view holds, that such an approximation is sufficient only for the description of the term system and electronic configuration of the completed and undisturbed molecule, but is not a sufficient basis for the theory of valency. According to this conception, true covalent linkage in normal molecules of the first order (as distinct from genuine complex salts and organic ring structures) is due to the formation of pairs of electrons, one from each atom; the bonding effect is mainly due to the degeneracy owing to the equality of the electrons and the bonds are strongly localized between two atoms. Various arguments of theoretical and experimental nature have been recently put forward in support of the latter view, and the present work was originally undertaken also in the hope of contributing to the evidence which ultimately will bring about a decision between these two concepts.

TABLE VIII

Molecule	Origin	Ground state			Excited state			Remarks
		ω''_1	ω''_2	ω''_3	ω'_1	ω'_2	ω'_3	
SO	ν_0 39109	—	1118	—	—	623	—	—
SO ₂	—	525	1150	1360	—	—	—	Raman and infra-red spectra
	33303	—	1128	1365	—	662	876	Band spectrum
SeO	33167	—	910	—	—	513	—	—
SeO ₂	32560	—	901	1189	—	663	790	—

From this point of view the most interesting result is that the vibrational frequencies of the normal and the excited states of SeO occur again almost unchanged in the symmetric valence vibration of SeO₂ in its normal and its excited states. Also the ν_0 of the diatomic and the corresponding triatomic molecules are similar. This is exactly the same behaviour as observed earlier in the case of SO and SO₂, and we are now able to combine the results of both analyses in Table VIII (all figures in cm⁻¹).

* Cf. literature mentioned by Lessheim and Samuel, *loc. cit.*, and Samuel, 'Current Sci.,' vol. 4, April (1936).

The values of ω'' and ω' of the diatomic molecule agree, indeed, very well with those of ω''_2 and ω'_2 of the corresponding dioxide. The slight increase of the values has to be expected since the repulsive force between the two O atoms of the dioxide slightly weakens the bond energy and therefore probably slightly increases the internuclear distance. With SO₂ it was possible to show that the molecule undergoes a considerable change of form on excitation and cannot be considered any longer isosceles. That the agreement between the vibrational frequencies of the diatomic and the corresponding triatomic molecule is not quite so good in the excited state will be due to this change. The value of the anharmonic constant for the symmetric valence vibration of SeO₂ in the unexcited state is also very close to that of SeO. A definite value cannot be given because only three vibrational levels are observed. The value, however, obtained from these levels being 5.5 cm^{-1} , in fair agreement with $\omega x = 6 \text{ cm}^{-1}$ of SeO, we may conclude that the order of magnitude will be the same.

These considerations are corroborated by thermochemical measurements. The heat of formation of solid SeO₂ from solid Se + gaseous O₂ is 57.1 k cal/mol . The atomic heat of formation is obtained according to Born's cycle by adding to this value the energy of dissociation of O₂ (117 k cal/mol), the heat of sublimation of solid Se (24 k cal/gm atom), one-half of the energy of dissociation of Se₂ (the vapour consisting of Se₂ molecules until above 1000° C), and finally deducting the energy of sublimation of solid SeO₂. The latter not being known we roughly measured the point of sublimation as about 470° C . According to Forcrand's rule,* this corresponds to a value for the latent heat of vaporization of about 22 k cal . The dissociation energy of Se₂ is $2.63 \text{ volts} = 59.3 \text{ k cal/mol}$ obtained in exactly the same way as mentioned above for S₂ from the convergence point of the absorption spectrum of Se₂ ($30874 \text{ cm}^{-1} = 3.81 \text{ volts}$) and the measured value of the ¹D term of Se (1.18 volts).† From these figures we obtain 205 k cal/mol as the atomic heat of formation of SeO₂ or $102.5 \text{ k cal/mol} = 4.45 \text{ volts}$ for each Se = O double bond. This value is as near to the dissociation energy of the SeO molecule, measured spectroscopically to 4.2 volts , as the estimated energy of sublimation of SeO₂ permits. This result is not surprising, since it has been shown recently‡ from the absorption spectra of the vapours of the chlorides and oxychlorides of sulphur, that the bond energy of the

* Forcrand, 'C.R. Acad. Sci. Paris,' vol. 133, pp. 268, 513 (1901).

† Rao and Krishnamurti, 'Proc. Roy. Soc.,' A, vol. 145, p. 694 (1934).

‡ Asundi and Samuel, 'Proc. phys. Soc. Lond.,' vol. 48, p. 28 (1936).

S—Cl, the $S = 0$ and the S=S bond remains practically unchanged in such widely different molecules as S_2 , SO, SCl_2 , $SOCl_2$, S_2Cl_2 , and SO_2 .

The above thermochemical calculations also show that the bond energy of the $Se = O$ bond remains the same in the molecules SeO and SeO_2 , and we may therefore take this as characteristic for molecules formed by atoms of the sixth group as long as they remain di- or tetravalent, *i.e.*, as long as the s^2 group of electrons remains on atomic orbitals. The linkage is brought about, then, by the four p -electrons only and the ground state of the triatomic molecule arises probably directly from the ground state of the diatomic one.

To our mind these spectroscopical results, supported by thermochemical considerations, indicate clearly a strong localization of the bonds. This conclusion could not be drawn with any certainty, if we would consider the corresponding vibrations of the unexcited molecules only. Indeed, the fact that empirical rules, like Morse's $\omega r^3 = \text{constant}$ for a large group of diatomic molecules exist in band spectroscopy shows already that ω is more sensitive to the moment of inertia and less sensitive to the bond energy. We know, indeed, that ω'' is almost the same for the radical OH and the OH^- ion with different electronic configurations or for N_2 and CO in spite of the fact that the energy dissociation of N_2 is much smaller than that of CO.

Therefore, conclusions on the number of valencies or the nearly related bond energies based on Raman and infra-red spectra alone, should be drawn with great caution only, as the factor of anharmonicity is of equal importance. In our case, however, there is correspondence between the harmonic frequencies not only of the ground state but also of the excited state and furthermore between the energies of excitation and for the ground state; even between the anharmonic constants. Even after the excitation of the molecule, *i.e.*, after one electron is transferred to a higher quantum group, the two ω' values remain almost equal. Finally, the determination of the energy of dissociation of SeO makes it possible to compare it with the bond energies of SeO_2 . This shows, indeed, that only one of the two double bonds between Se and O or between S and O seems to take part in the process of excitation, that only one of the corresponding internuclear distances is increased in this process, and that the energy of excitation seems to be accumulated in only one of the two double bonds. The two double bonds seem to act quite independently of each other. Described from the view point of the concept of the single-electron-bond interpretation of the method of molecular orbitals, the linkage of two atoms of the sixth group is characterized (Herzberg, Mulliken) by eight electrons, forming three pairs of bonding and one pair of anti-bonding electrons, thus giving two valencies. The same number of

valencies is obtained in the electron pair bond interpretation of the method of molecular orbitals in quite a different way. Here only those pairs are counted whose electrons originate in different atoms and therefore two pairs are obtained irrespective of the presence of the two other pairs, one of which originates in our case from Se atoms only and the other from the O atom alone (Hund's method of counting). That pair of *p*-electrons which does not take part in the linkage of SeO, because both electrons are originally Se-electrons, will form again two bonding pairs together with two electrons of the second O atom in SeO₂, and therefore this theory describes indeed the linkage of the Se = O bond in SeO and SeO₂ in a completely identical manner. In the single-electron bond interpretation, however, the linkage of SeO₂ is entirely different from that of SeO. Firstly, the antibonding electrons of SeO most probably become bonding electrons in SeO₂ and the linkage between each of the O atoms and the central atom is now made up of three bonding pairs and resembles the linkage of CO, which is indeed described as a triple bond in this theory. This distinction between the two SeO bonds in SeO₂ is, however, already an approach to the conception of localized bonds, and we shall not consider this as an argument. But if all non-localized electrons on molecular orbitals contribute towards the linkage, the bond of SeO is brought about by eight electrons in the field of two nuclei, and that of SeO₂ by twelve electrons in the field of three nuclei. These are two completely different cases. Why the bond energies, the energy of excitation, the anharmonic constant of the ground states, and the frequency of the symmetric valence vibration remain almost unchanged in SeO and SeO₂ cannot, therefore, be explained on the basis of non-localized bonds without great difficulties, whereas it is almost the natural outcome of the conception of localized bonds.

SUMMARY

The emission spectrum of SeO and the absorption spectrum of SeO₂ are analysed. The energy of excitation and the energy of the Se = O bond are almost identical in SeO and SeO₂, and the vibrational frequencies of SeO have almost the same values as the frequencies of the symmetric valence vibration of SeO₂, both in the normal and the excited state. The same is true about the corresponding anharmonic constants of the two unexcited molecules; that of excited SeO could not be measured.

The results indicate strong localization of the two Se = O bonds in SeO₂.

The analysis of the band system of SeO₂ is in complete agreement with Herzberg and Teller's theoretical selection rule for $\Delta v_{(\text{antisym})}$ for polyatomic molecules.

5105.6

3247.5

3060
OH

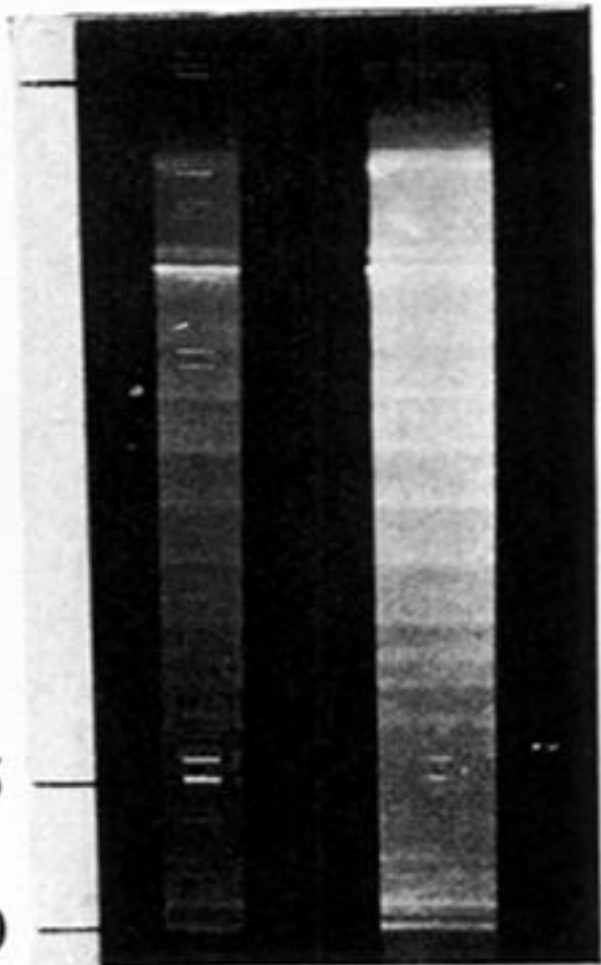


FIG. 1.

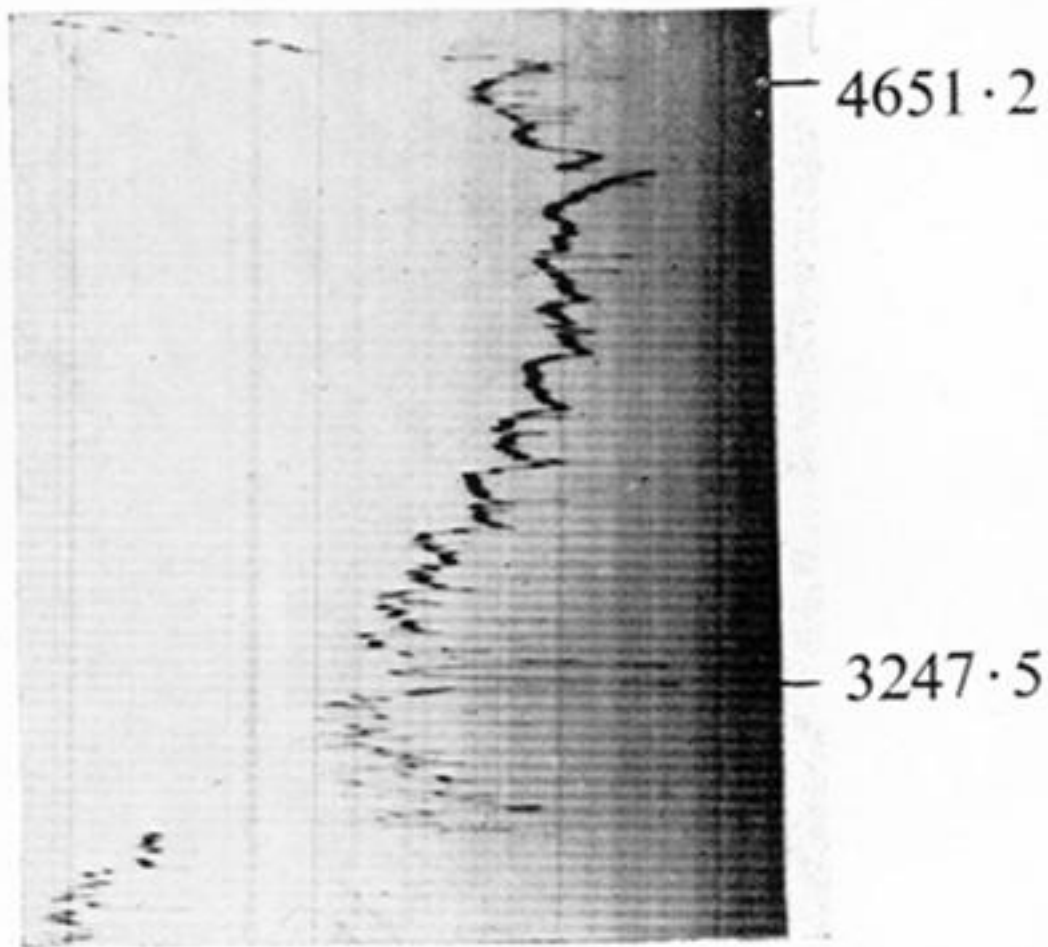


FIG. 2.

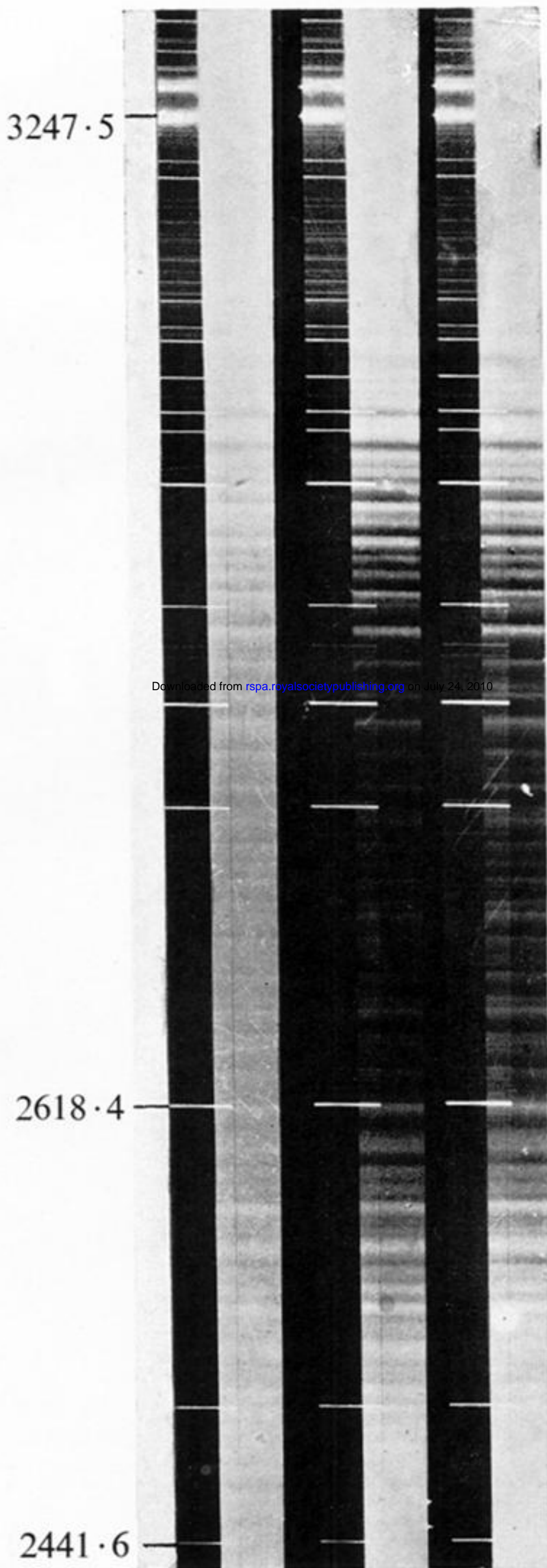


FIG. 3.

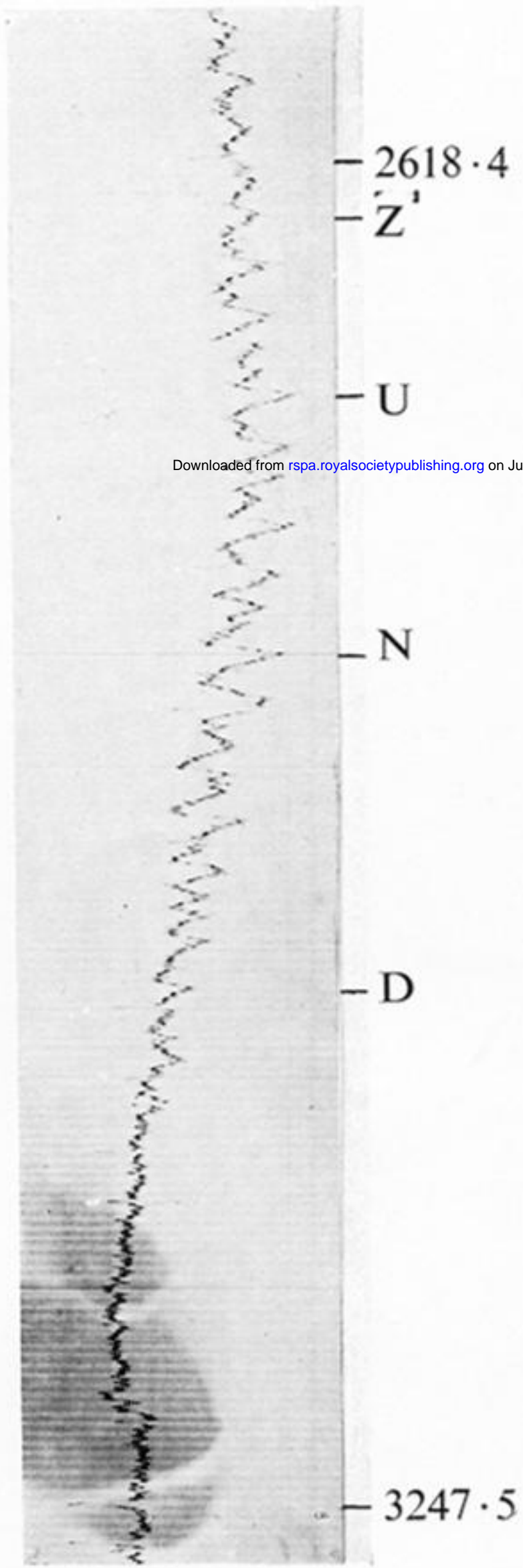


FIG. 4.

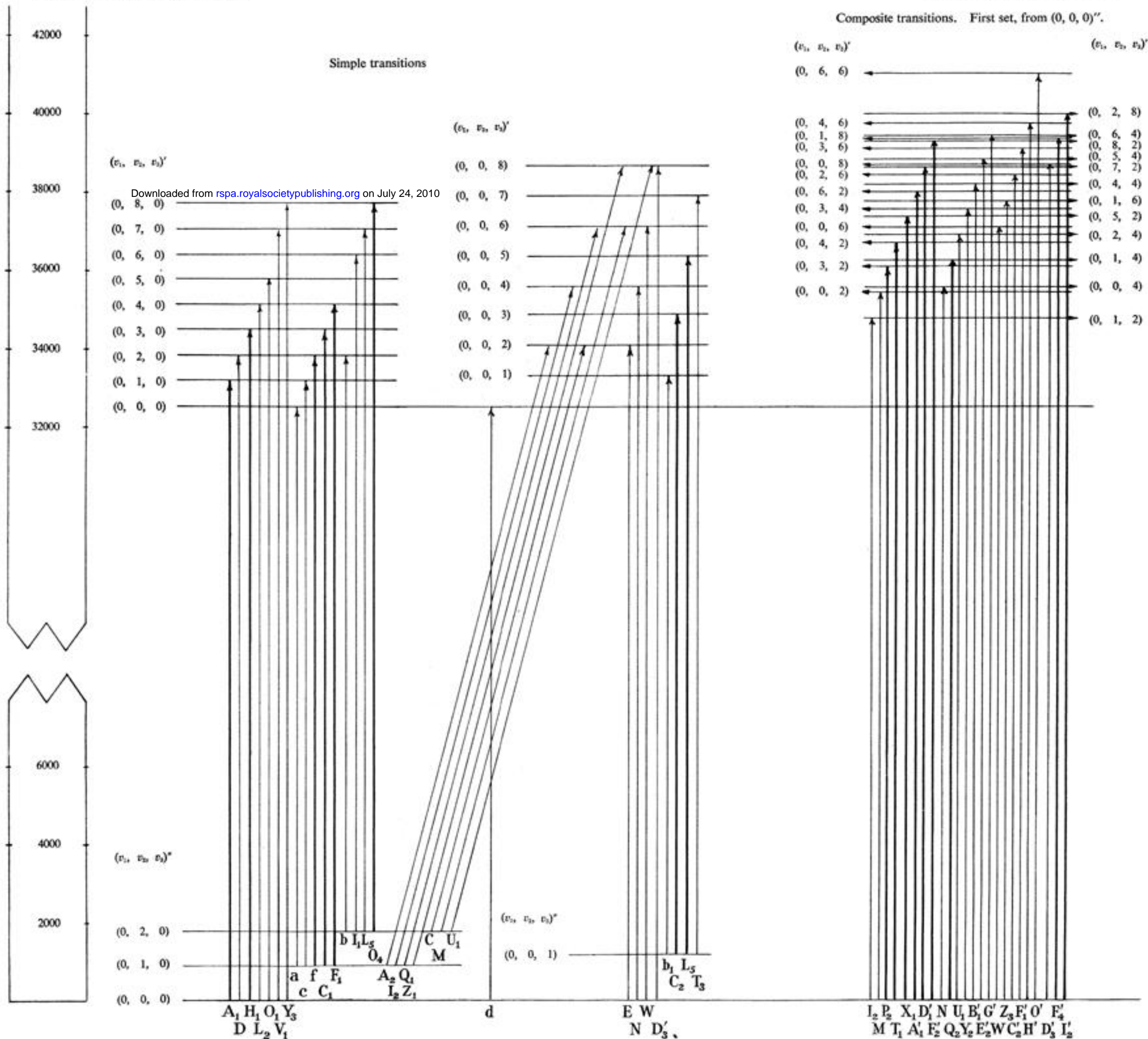


FIG. 5.