

THE NEAR ULTRA-VIOLET ABSORPTION BANDS OF SO₂.

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The absorption bands of SO₂ have been measured and the number of recorded bands considerably increased. The analysis of this band system is still to a large extent arbitrary and several arrangements of the bands are possible. Since, however, the symmetric valence vibration of unexcited SO₂, as known from Raman Effect and infra-red spectrum, has nearly the same value as the vibration of the molecule SO, known from its band spectrum, preference is given to an arrangement of the SO₂ bands, by which the symmetric valence vibration of excited SO₂ gains almost exactly the same values as that of excited SO.

THE absorption bands of sulphur dioxide in the near ultra-violet have been studied in more recent years by several authors. Dutta¹ obtained a small number of the bands whereas Watson and Parker² reported a large number of them. Dutta's analysis covers only a limited number of bands even among the bands obtained by him, whereas that of Watson and Parker is open to serious objections as pointed out by Dutta and later workers. The most serious is certainly that they obtain three different origins which is obviously impossible. Clements³ has given a new analysis of the bands recently. He has chosen a rather weak band at 31945 cm.⁻¹ as the (0, 0, 0)'' → (0, 0, 0)' transition on account of its behaviour under different temperatures. It should be possible indeed to single out the (0, 0, 0)'' → (0, 0, 0)' band on these considerations of changes in intensity with temperature. But the particular procedure adopted by him contains a number of theoretical and experimental simplifications and therefore 31945 cm.⁻¹ is not the only possible value for this transition. We have shown in this paper that the subsidiary maxima which accompany the main ones are also independent bands. Therefore intensity measurements become even more difficult because such subsidiary maxima can arise in quite different ways, *e.g.*, by a complete overlap of a strong broad band and a weak one or by the partial overlap of two narrow bands of about equal intensity. Clements has divided the bands into two different groups—the low frequency group and the high frequency group. The high frequency group consists of composite transitions to the vibrational levels of two modes of vibrations in the excited state of the molecule from the vibrationless state of the ground level, while the low frequency group arises

from transitions from the vibrational levels of the excited state of the ground frequency 525 to various vibrational levels of the normal state of the molecule. This division of the bands into two distinct groups means physically that the excited vibrational levels of the ground term of the two modes 525 and 1144, which are used for the explanation of the low frequency bands, do not combine with the excited vibrational levels of the excited terms of the 1144 mode, which are used for the explanation of the high frequency bands. Theoretically a selection rule which forbids such transitions is of course not known. We have observed the bands during our study⁴ of the absorption of the chlorides and oxychlorides of sulphur under different conditions. We rather think it likely that all the bands are more intimately connected with one another. To our mind there are also some other reasons which go against the analysis proposed by Clements. Firstly, according to the Franck-Condon diagram, we would not expect the band at the origin to be just one of the weakest, unless of course there is an abnormal change in internuclear distances on excitation. Secondly, he obtains in the excited state of the molecule, the frequency of symmetric deforming vibration decreased while that of the symmetric valence vibration increased. On the other hand, we have found a possibility of a different analysis which has a certain advantage. It is well known from infra-red and Raman spectra⁵ that in SO₂ the symmetric valence vibration has about the same value as that of SO in the ground state, which again agrees with the fact that the energy of the S=O band remains very nearly constant.⁴ In the analysis proposed here, also the symmetric valence vibration in the excited state of SO₂ is of the same order of magnitude as that of the excited state of SO. At the same time our analysis interprets the bands as a uniform system, *i.e.*, those on the high frequency side as due to transitions from the lower vibration levels of the ground state and those on the low frequency side as transitions from higher vibrational levels of the ground state.

Experimental.

The bands were obtained in the usual way with the apparatus described elsewhere⁴ at different temperatures and pressures. Spectrograms were taken with pure SO₂ and with SO₂ in the presence of other vapours like SCl₂, SOCl₂, etc. The plates were run on the recording microphotometer with different enlargements. The microphotograms were then measured by an Abbe comparator, and thus the bands as well as the standard lines which were also present on the microphotogram were directly compared. Several microphotograms were measured and the wave-lengths of the bands calculated by the usual Hartmann dispersion formula agreed to 0.3 A.U. The mean value of the wave-lengths was then taken so that the accuracy obtained was within

5 to 7 cm^{-1} . This allowed us to include also such bands which appear as subsidiary maxima due to overlapping. Only such subsidiary maxima, as were common to all the plates measured, have been included. On the still shorter wave-length side where the bands become diffuse, it was not possible to identify with certainty more bands than are tabulated here. Clements, however, has measured a few additional bands in this region which probably can be included in the present analysis within the error of his measurements. Table I gives the list of bands and Fig. 1 (Plate I) is a sample photometer curve. The lower frequency bands have not been measured but the values given by Clements are utilised for the time being to show that it is possible to extend the present analysis to them.

TABLE I.

λ (A.U.) in air	ν vac	Classification
3131.3	31926 A ₁	(0, 1, 2)" \rightarrow (0, 1, 2)'
3130.3	31937 A ₂	(0, 0, 2)" \rightarrow (0, 2, 0)'
3107.8	32168 B	(0, 1, 0)" \rightarrow (0, 0, 0)'
3087.6	32378 C ₁	(0, 2, 0)" \rightarrow (0, 2, 0)'
3086.2	32393 C ₂	(0, 0, 2)" \rightarrow (0, 0, 2)'
3067.9	32586 D ₁	(0, 1, 2)" \rightarrow (0, 2, 2)'
3066.0	32606 D ₂	(0, 0, 2)" \rightarrow (0, 3, 0)'
3046.3	32817 E ₁	(0, 0, 1)" \rightarrow (0, 0, 1)'
3044.6	32836 E ₂	(0, 1, 0)" \rightarrow (0, 1, 0)'
3043.8	32844 E ₃	(0, 2, 0)" \rightarrow (0, 0, 2)'
3025.0	33048 F ₁	(0, 2, 0)" \rightarrow (0, 3, 0)'
3023.4	33066 F ₂	(0, 0, 2)" \rightarrow (0, 1, 2)'
3005.8	33259 G ₁	(0, 0, 2)" \rightarrow (0, 4, 0)'
3001.9	33303 G ₂	(0, 0, 0)" \rightarrow (0, 0, 0)'
2985.4	33487 H	(0, 1, 0)" \rightarrow (0, 2, 0)' or (0, 0, 1)" \rightarrow (0, 1, 1)'

λ (A.U.) in air	ν vac	Classification
2966.5	33700 I ₁	(0, 2, 0)" \rightarrow (0, 4, 0)' or (0, 0, 2)" \rightarrow (0, 2, 2)'
2964.8	33719 I ₂	(0, 0, 1)" \rightarrow (0, 0, 2)'
2962.7	33743 I ₃	(0, 2, 0)" \rightarrow (0, 0, 3)' or (0, 1, 0)" \rightarrow (0, 1, 1)'
2946.6	33928 K ₁	(0, 0, 1)" \rightarrow (0, 3, 0)'
2944.9	33947 K ₂	(0, 1, 0)" \rightarrow (0, 0, 2)'
2943.7	33961 K ₃	(0, 0, 0)" \rightarrow (0, 1, 0)'
2926.8	34157 L ₁	(0, 1, 0)" \rightarrow (0, 3, 0)'
2924.4	34185 L ₂	(0, 0, 0)" \rightarrow (0, 0, 1)'
2908.8	34368 M	(0, 0, 2)" \rightarrow (0, 3, 2)'
2889.1	34603 N ₁	(0, 0, 1)" \rightarrow (0, 0, 3)'
2888.3	34612 N ₂	(0, 0, 0)" \rightarrow (0, 2, 0)'
2869.0	34845 O	(0, 1, 0)" \rightarrow (0, 0, 3)' or (0, 0, 0)" \rightarrow (0, 1, 1)'
2853.7	35047 P ₁	(0, 0, 2)" \rightarrow (0, 4, 2)'
2850.0	35078 P ₂	(0, 0, 0)" \rightarrow (0, 0, 2)'
2833.3	35284 Q	(0, 0, 0)" \rightarrow (0, 3, 0)'
2819.1	35462 R ₁	(0, 0, 2)" \rightarrow (0, 2, 4)'
2817.5	35482 R ₂	(0, 2, 0)" \rightarrow (0, 4, 2)'
2800.3	35700 S	(0, 1, 0)" \rightarrow (0, 0, 4)'
2781.0	35948 T ₁	(0, 0, 0)" \rightarrow (0, 4, 0)'
2779.3	35970 T ₂	(0, 0, 0)" \rightarrow (0, 0, 3)'
2766.3	36139 U	(0, 0, 2)" \rightarrow (0, 3, 4)'
2747.3	36389 V	(0, 0, 0)" \rightarrow (0, 2, 2)'
2681.1	37287 W	(0, 0, 0)" \rightarrow (0, 2, 3)'

TABLE II.

	(0, 0, 0)"		(0, 1, 0)"	
(0, 0, 0)'	31937 A ₂ 458	1136	(30801) 440	1109
(0, 1, 0)'	32393 C ₂ 451	1152	(31241) 478	1102
(0, 2, 0)'	32844 E ₃ 459	1125	(31719) 449	1137
(0, 3, 0)'	33303 G ₂ 440	1135	32168 B 438	1140
(0, 4, 0)'	33743 I ₃ 442	1137	32606 D ₂ 460	
(0, 5, 0)'	34185 L ₂ 427	1119	33066 F ₂ 421	1140
(0, 6, 0)'	34612 N ₂ 466	1125	33487 H 441	1109
(0, 7, 0)'	35078 P ₂ 404	1150	33928 K ₁ 440	1092
(0, 8, 0)'	35482 R ₂ 466	1114	34368 M 477	1109
(0, 9, 0)'	35948 T ₁ 441	1103	34845 O 439	1126
(0, 10, 0)'	36389 V	1105	35284 Q 416	1127
(0, 11, 0)'	—		35700 S 439	1097
(0, 12, 0)'	—		36139 U	1092
(0, 13, 0)'	—		—	

Analysis.

The analysis of the bands of a polyatomic molecule, in the state of development, is still to a large extent arbitrary. The total number

and the possible modes of vibration give entirely different possibilities of arrangement. The Raman and infra-red frequencies are of course the guiding factors so far as the ground state of the molecule is concerned, but how these frequencies will be affected as regards intensity and magnitude in the excited

TABLE III.
 ω_3'' , ω_3' frequencies.

	(0, 0, 0)''		(0, 0, 1)''		(0, 0, 2)''
(0, 0, 0)'	33303 G ₂ (882)	1366	<u>31937 A₂</u> (880)		
(0, 0, 1)'	<u>34185 L₂</u> (893)	1368	32817 E ₁ (902)	1310	<u>(31507)</u> (886)
(0, 0, 2)'	35078 P ₂ (892)	1859	<u>33719 I₂</u> (883)	1326	32393 C ₂
(0, 0, 3)'	<u>35970 T₂</u>	1368	34602 N ₁ (860)		
			<u>35462 R₁</u>		

TABLE IV.
 ω_2'' , ω_2' frequencies.

	(0, 0, 0)''		(0, 1, 0)''		(0, 2, 0)''
(0, 0, 0)'	33303 G ₂ (658)	1135	32168 B (668)	1103	(31065) (654)
(0, 1, 0)'	33961 K ₃ (651)	1125	32836 E ₂ (651)	1117	(31719) (659)
(0, 2, 0)'	34612 N ₂ (672)	1125	33487 H (670)	1109	32378 C ₁ (670)
(0, 3, 0)'	35284 Q (664)	1127	34157 L ₁		33048 F ₁ (652)
(0, 4, 0)'	35948 T ₁				33700 I ₁

states of the molecule cannot be predicted with any certainty. In SO_2 in the normal state, three frequencies corresponding to three fundamental modes of vibration are known from Raman and infra-red spectra.⁵ These are 525 cm.^{-1} for the symmetric deforming vibration ω_1'' , 1146 to 1150 cm.^{-1} for the symmetric valence vibration ω_2'' , and 1340 to 1360 cm.^{-1} for the anti-symmetric valence vibration ω_3'' . This correlation of the modes of vibration and the triangular shape of the molecule are confirmed by the depolarisation of the Raman frequency 1340 cm.^{-1} . The infra-red spectrum indicates 122° as the OSO angle in the ground state. If we accept the band at about 31945 cm.^{-1} as the origin of the system according to Clements, it is possible by using

TABLE V.

$0, 0, \nu_3'$	$(0, 1, 0)''$	$0, \nu_2', 0$	$(0, 0, 1)''$
0	32168 B (898)	0	31937 A ₂ (669)
1	33066 E ₂ (881)	1	32606 D ₂ (653)
2	33947 K ₂ (898)	2	33259 G ₁ (669)
3	34845 O (855)	3	33928 K ₁
4	35700 S		
	$(0, 2, 0)''$		$(0, 0, 2)''$
0	(31065) (880)	0	
1	(31945) (899)	1	(31280) (657)
2	32844 E ₃ (899)	2	31937 A ₂ (660)
3	33743 I ₃ (860)	3	32586 D ₁
4	34603 N ₁		

TABLE VI.
Composite Transitions.
Transitions from normal state.

v_2'	$(0, v_2, 0)'$		$(0, v_2, 1)'$		$(0, v_2, 2)'$		$(0, v_2, 3)'$
0	33303 G ₂ (658)	882	$\overline{34185 L_2}$ (660)	893	35078 P ₂ (664)	892	$\overline{35970 T_2}$ (683)
1	33961 K ₃ (651)	884	$\overline{34845 O}$ (637)	897	(35742) (647)	911	$\overline{(36653)}$ (634)
2	34612 N ₂ (672)	870	$\overline{35482 R_2}$ (657)	907	36389 V	898	$\overline{37287 W}$
3	35284 Q (664)	(855)	$\overline{36139 U}$				
4	35948 T ₁						

the additional bands measured by us on the high frequency side to arrange all of them in such a way that they represent transitions from the vibrational levels of ω_2'' to the levels of ω_2' (*vide* Table II). It will be seen that this gives 1112 cm.⁻¹ for ω_2'' in agreement with the Raman frequency 1146 cm.⁻¹ and 458 cm.⁻¹ for ω_2' . This means that in the excited state of the molecule, the deforming and the symmetric valence vibrations show a uniform decrease in frequency. Thus one of the objections to the earlier analysis would be removed but the objection that the bands form, as it were, two distinct groups in the two regions, remains. Furthermore, the origin will be represented by a weak band, and on the high frequency side there will not be a single band due to a combination transition, involving more than one vibrational mode of the same electronic state.

We have therefore tried a new analysis of the bands on the high frequency side with the idea to test if it is possible to obtain an analysis which introduces for the symmetric valence vibration in the excited state of the molecule a frequency near to that of the excited SO molecule because already in the ground state ω_2'' with 1150 cm.⁻¹ is very near to 1118 cm.⁻¹ the frequency of SO in the ground state. Indeed, by taking 33303 cm.⁻¹ as the origin it has been possible to arrange the bands so that all the bands on the high frequency side are represented as transitions from the low vibrational levels

of the two modes of vibration ω_2'' and ω_3'' to each of the vibrational levels of ω_2' and ω_3' separately and in combination. Tables III to VI contain the analysis and Fig. 2 gives the schematic representation of most of the transitions observed. All the bands have been classified though a few appear to justify classification in two ways. These are also shown in Table I. (The bands in square brackets will be discussed later.) To test whether this analysis can be extended to the low frequency bands listed by Clements we have tried to fit in some of these bands $\dagger\dagger$ as due to transitions arising from the higher vibrational levels of the ground state. This, indeed, appears to be possible as can be seen from the following few examples:—

TABLE VII.

Clements ν in cm.^{-1}	Transition
31926	$(0, 0, 2)'' \rightarrow (0, 2, 0)'$
31719	$(0, 2, 0)'' \rightarrow (0, 1, 0)'$
31280	$(0, 0, 2)'' \rightarrow (0, 1, 0)'$
31065	$(0, 2, 0)'' \rightarrow (0, 0, 0)'$
30801	$(0, 1, 2)'' \rightarrow (0, 2, 0)'$
29692	$(0, 2, 2)'' \rightarrow (0, 2, 0)'$

These bands are included in Fig. 2. We feel confident therefore that by using one or two more vibrational levels both in the lower and upper states and with the possibility of combination and composite bands, it will be possible to apply the present analysis to the whole system of bands. This means then, that the bands on the low frequency side are simply an extension of the other bands and the decrease in intensity follows gradually and closely the excitation of the vibrational levels of the ground state. Incidentally, those bands which appear at the extreme end of the visible region will be correlated to higher vibrational levels of the ground level. We intend to continue our work with higher dispersion and greater pressure under different temperatures.

We have not got enough vibrational levels to obtain definite formulæ for the vibrational functions; this we propose to do later when work on the lower frequency bands is completed. But it can be seen that we obtain

$\dagger\dagger$ These are included in () brackets in Tables II to VI.

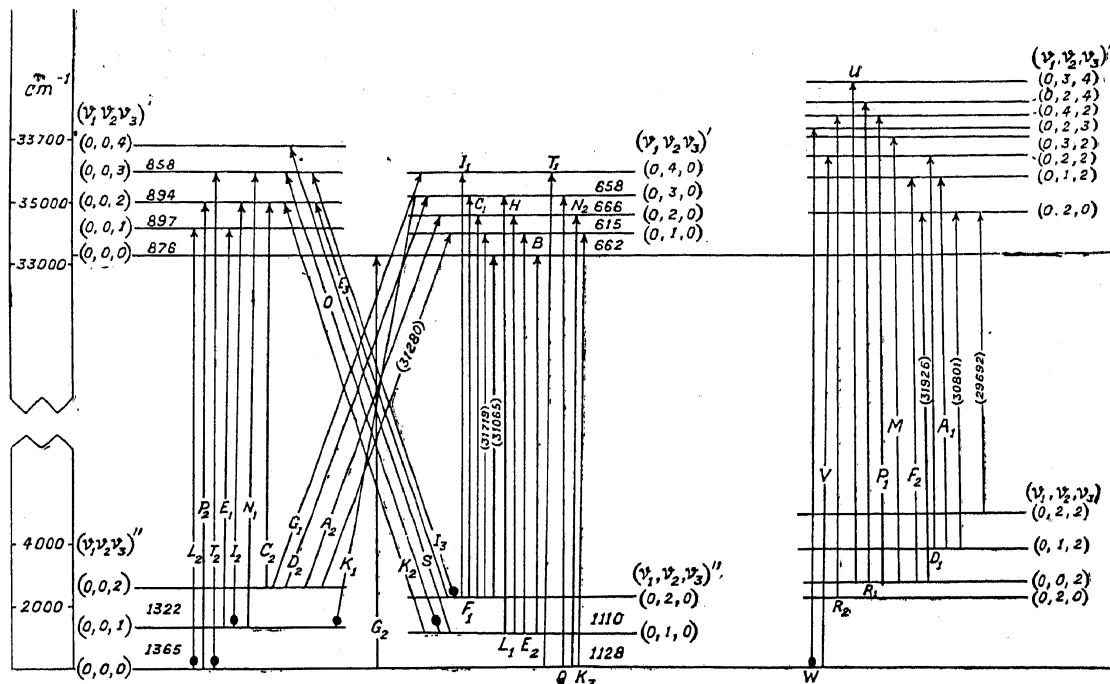


FIG. 2.

ω_2'' and ω_3'' in the ground state and the same two modes of vibration, both with decreased frequency in the excited state of the molecule. These are summarised in Table VIII.

The few vibrational levels in the ground state show decrease in spacing but those in the excited state are not regular. We are not sure how far this is genuine because far from measuring the origins of the bands, here we do not measure even the heads of the bands but only the point of maximum intensity in each band. Even these points of maximum intensity are affected by the overlap of neighbouring band heads. In general, however, the distribution of intensity is more or less normal. The bands may be taken to follow regular progressions, the confused appearance observed by earlier workers being merely due to two modes of vibration being intermixed and to the fact that the 220 cm.⁻¹ frequency sought for is not genuine but is roughly the difference between ω_3' and ω_2' , which therefore cannot be constant.

The relation between the frequencies of vibration of SO and those of SO₂ is given in Table IX.

This relation indicates that the distance between S and one of the oxygen atoms is increased in the excited state of SO₂, in the same manner as the internuclear distance increases with decreasing ω , on excitation of SO. It appears as if SO₂ in the excited state is no longer isosceles. This agrees with the change in the valency angle OSO, found by Jonescu⁶ on a partial rotational analysis of the SO₂ bands. The valency angle of SO₂ decreases from 122° in

TABLE VIII.

Mode of vibration	Level	cm. ⁻¹
ω_2''	0	0
	1	1128
	2	2238
ω_2'	0	0
	1	662
	2	1312
	3	1978
	4	2636
ω_3''	0	0
	1	1365
	2	2687
ω_3'	0	0
	1	876
	2	1773
	3	2667
	4	3525

TABLE IX.

	SO	SO ₂	
	Band Spectra	Infra-red Spectrum	Band Spectra
Unexcited ..	1118	525, 1150, 1360	1128, 1365
Excited ..	623		662, 876

the normal to 96° in the excited state.^{6,7} Herzberg and Teller⁸ have deduced a rigorous selection rule according to which the antisymmetric frequency should appear if at all as a weak one and only transitions involving an even change between its vibrational levels in the excited and lower electronic states should occur. In the case of a considerable change of internuclear distance on excitation, the rule might be violated in such a manner that also transitions with odd changes in vibrational quantum numbers can take place. But in this case they have to be weak and the transitions should lead either to a forbidden electronic level or to one which involves a forbidden component of electric moment. Since in this case the form of the molecule is completely changed, no definite prediction can be made unless rotational analysis is completed. Furthermore to account for the diffuseness of the bands at shorter wave-lengths which in this case cannot be produced by predissociation for energetical reasons, Franck, Sponer and Teller⁹ have assumed that a second electronic level is very near the excited state involved in these bands. Thus a degeneration of the final state of the bands or of certain of its vibrational levels is quite possible.

The analysis given in Tables III, V and VI includes a number of transitions which are forbidden if Herzberg and Teller's selection rules are rigorously valid. These are included in square brackets and some of them appear by no means to be weak. It is, however, possible to classify some of them in such a way that the selection rule is not violated. This is shown in Table X. Fig. 2 displays such of the bands in square brackets as can be classified without violation of Herzberg and Teller's selection principle, as due to the non-forbidden transition. It can be seen that of the seven bands which cannot be classified otherwise (these are marked in Fig. 2) four are either diffuse or weak but three are not so. Too much importance should, however, not be attributed to intensity considerations because as already pointed out above, the main maximum of the envelope of several overlapping bands may be produced in quite different ways and may be due as often as not, to a weak band superimposed on the ascent of a stronger one. This obtains particularly to the group of bands I, since this is a very narrow band made up of at least three different bands. In reality only the band O, one of the few which is not resolved, appears to go against the selection rule. In view of all these considerations, experimental evidence is not definite to decide whether the selection rule is obeyed or violated on account of either degeneration or the complete change which the molecule undergoes on excitation.

It is, however, strange, that the deforming vibration does not appear at all in this electronic transition although it is also a total symmetrical vibration. *A priori* there is nothing known about the frequency of

TABLE X.

Band	Forbidden transition	O—C	Non-forbidden transition	O—C	Remarks
31937 A ₂	(0, 0, 1)" (0, 0, 0)'	- 1	(0, 0, 2)" (0, 2, 0)'	+ 9	In this case band 31926 A ₁ can be classified as (0, 1, 2)" (0, 1, 2)', the O—C value being +3.
32606 D ₂	(0, 0, 1)" (0, 1, 0)'	+ 6	(0, 0, 2)" (0, 3, 0)'	+12	In this case 32586 D ₁ can be classified as (0, 1, 2)" (0, 2, 2)' with O—C = +13.
33066 F ₂	(0, 1, 0)" (0, 0, 1)'	+15	(0, 0, 2)" (0, 1, 2)'	+15	
33259 G ₁	(0, 0, 1)" (0, 2, 0)'	+ 9	(0, 0, 2)" (0, 4, 0)'	+ 7	
33719 I ₂	(0, 0, 1)" (0, 0, 2)'	+ 8			} Narrow double superimposed.
33743 I ₃	(0, 2, 0)" (0, 0, 3)'	+11			
33928 K ₁	(0, 0, 1)" (0, 3, 0)'	+12			(Weak).
34185 L ₂	(0, 0, 0)" (0, 0, 1)'	+ 6			(Weak).
34845 O	(0, 1, 0)" (0, 0, 3)'	+ 3			(Not weak).
35462 R ₁	(0, 0, 1)" (0, 0, 4)'	- 1	{ (0, 1, 1)" (0, 3, 3)' or (0, 0, 2)" (0, 2, 4)'	{ - 7 - 9 }	
35482 R ₂	(0, 0, 0)" (0, 2, 1)'	- 9	(0, 2, 0)" (0, 4, 2)'	- 8	
35970 T ₂	(0, 0, 0)" (0, 0, 3)'	0			(Weak).
36139 U	(0, 0, 0)" (0, 3, 1)'	-18	(0, 0, 2)" (0, 3, 4)'	-20	Diffuse, uncertain.
37287 W	(0, 0, 0)" (0, 2, 3)'	+ 5			Diffuse, uncertain.

deformation in the excited level, but in the unexcited it is 525 cm.⁻¹ We do not find any vibration in the excited level which might be considered as the

modified value of this frequency and there is certainly no band at a distance of 525 cm.^{-1} from the origin, which could be considered to be the $(1, 0, 0)^* \rightarrow (0, 0, 0)^*$ transition; similar multiples are also absent. In this respect the analysis proposed here certainly does not follow the rules developed by Herzberg and Teller and the question arises if the complete change of form and electric moment of the molecule does not permit even the approximate application of their theory. We have already pointed out, that at present the analysis of such bands is to a large extent arbitrary and it is of course possible to avoid this difficulty by selecting another band as the origin. But then we have to fall back on an analysis like that of Clements or rather the improved one given in the earlier part of this paper (Table II). It is possible then to introduce the total symmetric deforming vibration and to cancel the antisymmetric valence vibration altogether and thus remove all the difficulties mentioned above, but only at the expense of the objections already raised, particularly, the division of the bands into two distinct groups and the weak intensity of the band at the origin. For these reasons and on account of the similarity of ω_1' and ω_2' with the corresponding values for SO , we prefer the second analysis proposed here in the present state of the development of the theory of polyatomic molecules.

The agreement between the frequencies of the symmetric valence vibration in the ground and the excited states with the corresponding frequencies of the diatomic SO molecule is particularly interesting. From a large amount of chemical and physical evidence, it is known that the bonds in a polyatomic molecule can be approximately considered to be independent of one another. For example, the constant Raman frequencies, the constant values of dipole moments of the same group in different molecules, indicate this. It appears as if this holds good also in the excited state, and as if therefore, the electronic configuration of the one SO bond in SO_2 changes on excitation similarly like that in SO , quite independently of the other SO bond. The wave-mechanical interaction of the two electron pairs of the one double bond with the two of the other bond seems to be very weak and the bond appears to be strongly localised between S and O . Otherwise such a coincidence will be difficult to understand. It might not be too far fetched to suggest that the excited state of SO_2 is brought about by the combination of an unexcited SO molecule ($^3\Sigma^-$) and an excited oxygen atom (1D), even as the excited state of SO is formed by S (3P) + O (1D). That the energies of the bonds $S-Cl$, $S-O$ and $S-S$ remain almost unchanged if molecules like S_2 and SO possessing two free valencies combine with other atoms to form polyatomic molecule, e.g., S_2Cl_2 , $SOCl_2$, is already shown in discussions on the absorption and photodissociation of the chlorides and oxychlorides of sulphur.⁴

The analysis presented here further points out the independence of the bonds not only in the ground state but even in the excited state. At least for the ground state, it can be said that this appears to be rather general. Already a preliminary comparison of band spectroscopic data of diatomic molecules with those of the Raman and infra-red frequencies of polyatomic molecules, reveals a number of examples in which a similarity between the symmetric valence vibrations exists, analogous to the one that exists for internuclear distances.¹⁰ These data are collected in Table XI.

TABLE XI.

Raman effect or Infra-red			Band Spectra	
Molecule	Vibration	(cm. ⁻¹)	Molecule	ω_e
H ₂ O	Symmetric valence	3600	OH	3568
(OH) ⁻		3615	"	"
CH ₄	Total Symmetric valence	2915	CH	2851
SnCl ₄	"	365	SnCl	351
PH ₃	Valence P-H	2327	PH	~2380
BiCl ₃	" Bi-Cl(?)	289	BiCl	308
SOCl ₂	" S=O	1229	SO	1118
POCl ₃	" P=O(?)	1295	PO	1228
C ₂ H ₄	" C=C	1623	C ₂	1630

As the table shows this relation seems to hold good for non-linear polyatomic molecules with an even number of electrons.

Further investigations on this and related problems are in progress.

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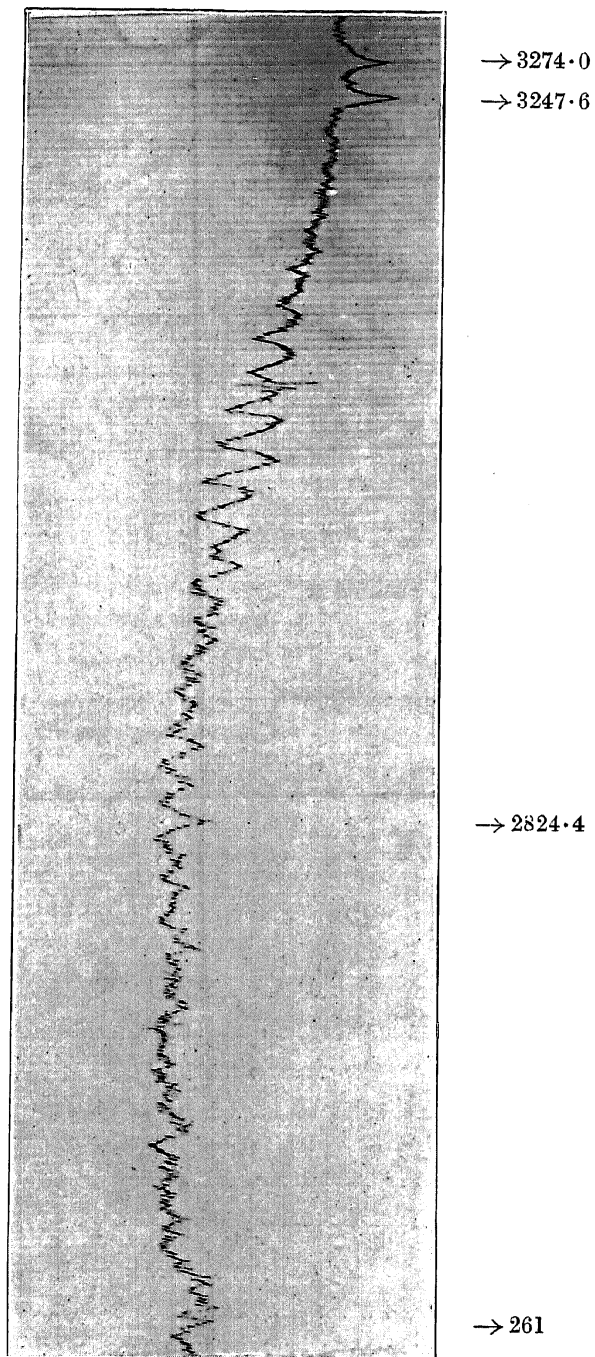


FIG. 1.