group of more or less unmixed peaks is likely to be found giving a clue to the proper assignment of the bands. Then the intermediate values of $(G_b-G_a)''$ serve as intensity checks on a proposed analysis.

If there exists a background of absorption from many unresolved weak bands or a continuous background which suffers temperature variation, only an examination leading to qualitative results may be feasible. Under such circumstances the line from which peak heights in the traces are measured (x_0) will have to be drawn from an appraisal of the condition present.

The writer wishes to thank Professor R. S. Mulliken for many consultations during the development of this discussion.

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On the Absorption Spectrum of Sulphur Dioxide

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An attempt to organize the absorption bands of sulphur dioxide in the region 3900–2600A has been made. The $(000)''-(000)'$ transition λ3129.5A (31,945 cm^{-1}) has been definitely located from a study of the temperature behavior of the lower frequency bands. Two of the vibrational frequencies known in the normal state have been observed and the intervals between successive lower levels determined. One of the frequencies in the excited state has been definitely assigned and a tentative value has been assigned for a second frequency. The configuration of the excited molecule is discussed.

Introduction

The spectrum of sulphur dioxide, a molecule known from its permanent dipole moment to be of triangular form[1] has attracted much attention. The normal modes of vibration of this type of molecule are well known.[2] If, as is very likely true of SO_2, the strong forces are those binding two atoms (here O) to a central atom (here S), the three frequencies can be classified as ν_2, a "deformation" frequency and ν_1 and ν_3, the symmetrical and unsymmetrical "valence" frequencies. The normal state of sulphur dioxide has been investigated from infrared and Raman data and the frequencies of the normal vibrations established with some certainty.[3]

Bands involving electronic transitions occur in the ultraviolet region of the spectrum and have been recognized as jumps to more than one excited electronic state. The more intensely absorbing higher frequency band system has been examined in emission and absorption by Chow,[4] in absorption by Jonescu[5] and at still higher frequencies by Wieland.[6] The lower frequency region, which is the subject of the present communication, has already been studied by Watson and Parker,[7] who arranged some of the observed absorption bands into series. These workers however used the older frequency for the ν_2 vibration of the molecule in the normal state; also they followed the formula for a diatomic molecule separately for the three modes of vibration, as has been pointed out by Dutta.[8] It thus seemed desirable to reexamine this portion of the spectrum. As a result of the present work, the $(0, 0, 0)''-(0, 0, 0)'$ band** has been located through detailed study of the temperature behavior of the various bands, using photo-

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[1] H. A. Stuart, Zeits. f. Physik. **59**, 13 (1929).

[2] D. M. Dennison, Rev. Mod. Phys. **3**, 180 (1931).

[3] For references see H. A. Stuart, *Molekulstruktur*, Springer, 1934.

[4] T. C. Chow, Phys. Rev. **44**, 638 (1933).

[5] A. Jonescu, Comptes rendus **197**, 35 (1933).

[6] K. Wieland, Nature **130**, 847 (1932).

[7] W. W. Watson and A. E. Parker, Phys. Rev. **37**, 1484 (1931).

[8] A. K. Dutta, Acad. Sci. U. P. India Bull. **1**, 89 (1931–32).

** A level of a molecule with three normal modes of vibration must be identified by three quantum numbers. These will be given in the order v_1, v_2, v_3, and that they belong to the excited or normal electronic state will be indicated by the prime and double prime, respectively.

graphs at various pressures, and a new analysis of the system is here proposed.

The present analysis has been facilitated by several recent developments. For one thing, the intensity problem for electronic-vibrational bands of the XY_2 type of molecule has been attacked by consideration of the extended Franck-Condon principle in the case of chlorine dioxide by Urey and Johnston[9] and recently by Ku.[10] Also, applications of the group theory[11] have led to the formulation of vibrational and electronic selection rules.

EXPERIMENTAL

Absorption spectra were taken with various tube lengths from 40 cm to 4 meters and pressures between 1 mm and 60 cm of mercury. A 40 cm tube with 1 mm pressure brought out the bands in the region 2900A while the 4 meter tube with 60 cm pressure was required for bands at 3900A. This intensity factor of several thousand necessitated the taking of a large number of plates. The light source was a continuous hydrogen discharge for the shorter wavelengths and a tungsten filament lamp in the longer wavelength region where the lines in the hydrogen source became troublesome. Many comparison pictures with the gas at two temperatures were taken in order to be able to assign with some assurance the lower vibrational states involved in the various transitions (see below). The temperature differences were usually about 40°C, spaced about room temperature, although some plates for ranges from -80°C to 600°C were taken. The instrument used was a Hilger E3 spectrograph which was well suited to the examination of the vibrational structure, inasmuch as plates taken in the first order of the 21-foot grating showed resolution insufficient to be of additional help.

On the plates the bands obtained were so broad as to render wavelength determinations with a comparator in the usual way liable to considerable error unless many re-settings were made. To avoid this necessity, the measurements were taken from microphotometer traces, which shaped the bands and further showed up "satellite peaks" difficult to measure directly. The traces gave also the comparison of intensities required for temperature variation information. In the absence of sharp edges, wavelength determinations were made of the points of maximum absorption for each peak. Lines or the edges of opaque paper strips gummed on the plate were used as reference marks, and the intervals between then were calibrated from the iron comparison spectrum by comparator measurements. The absorption peaks measured with a scale from the reference marks on the trace were then located on the calibration "distance-wavelength" chart. Such a graph was made for each plate as the dispersion was never exactly repeated in two exposures. A large number of plates under various conditions of exposure were measured and the frequencies taken from weighted averages; except where noted each value comes from three or more plates. The uncertainty with this procedure arises from averaging values for peaks resolved on one plate with values for the same peaks only partially resolved on other plates taken under slightly different pressures. However the values were consistent within about 15 cm^{-1}.

INTENSITY AND TEMPERATURE VARIATION

The use of the microphotometer as applied to the measurement of intensity changes with temperature in temperature variation of absorption spectra is discussed in the preceding paper.[12] Some of the complications encountered in practice have been more fully considered there. These may be summarized as unresolved rotational structure, overlapping of vibrational bands and the background of absorption arising from many weak bands. In spite of these embarrassments, temperature variation gave valuable clues to an arrangement of the band system.

In a gas whose molecules have only nondegenerate vibrational energy levels, the molecules are distributed among the latter according to the Boltzmann law $N_G = N_0 e^{-G''hc/kT}$. A temperature difference of 40°C is ample to show pronounced changes in intensities of absorption for bands in the spectrum of SO_2 coming from

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[9] H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931).

[10] Z. W. Ku, Phys. Rev. **44**, 376 (1933); **44**, 383 (1933).

[11] R. S. Mulliken, Phys. Rev. **43**, 279 (1933); L. Tisza, Zeits. f. Physik **82**, 48 (1933); A. V. Bushkovitch, Phys. Rev. **45**, 545 (1934).

[12] J. H. Clements, Phys. Rev. **47**, 220 (1935).

TABLE I. *Observed bands.*

ν	Intensity	$(G_b-G_a)''$ from Temp. Var.	
25188	0.02		
25733	.1	230	
26109	.2	140	
26253°			
26469	.1	220	
26609°			
26672	.3	60	
27005	.4	0 ←	
27355	.1	120	
27510	.2	200	
27594	.2	300	
27940	.2	250	
28200‡			
28296	.3	200	(1)
28466	.1	400	
28514	.1	400	
28588	.2	550	
28604°	.2		
28802‡			
28818	.2	150	
28910°			
29036	.3	400	
29095	.2	400	
29223	.2	470	
29300	.2		
29403	.2	400	
29447	.3	200	
29472°			
29522	.3		
29622	.3		
29656	.5		
29692	.6		
29742	.8		
29798‡			
29832	.9	0	
29896	.9	500	
29946	1.4	0 ←	
29967	1.2	500	
29994	1.2	1000	
30048	1.2	1000	(2)
30076	1.5	0	
30103	1.6	0	
30139	3.0	0	
30185	2	500	
30267	3	150	
30343‡			
30368	6	300	
30394‡			
30432‡			
30500	8	200	
30582	10	70	
30675	15	50	
30700‡			
30721°	20	0 ←	
30779‡			(3)
30801‡			
30855	25	60	
30895‡			
30970	40	40	
30985‡			
31028	40	40	
31065°			
31124	40	0	
31241‡			
31280‡			
31330	50	0	
31360‡			
31427	60	500	
31507	65		
31567	60		
31607‡			(4)
31646	120	500	
31719	100		
31767	80		
31793‡			
31858	90		
31926	200	200	
31945 A^{x}		0† ←	(5)
32161 B^{L}	300		
32377 *C*	600		
32607 *D*	800		
32850 *E*	1200		
33080 *F*	1700		
33313 *G*	2000		
33547 *H*	1900		
33760 *J*	2000		
33960 *K*	1700		
34030 *L*	1600		
34180 *M*	1600		
34200 *M′*	1600		
34241	700		
34396 *N*	1600		
34462 *N′*	900		
34488	400		
34620 *O*	1700		
34698	400		
34724	200		
34785	1000		
34846 *P*	1600		
34940°	100		
34970	500		
35053 *Q*	1800		
35133°			
35168	800	0	
35297 *R*	1500		
35390			
35474 *S*	1200		
35507 *T*	1200		
35532°			
35634	300		
35682	700		
35742 *U*	1500		
35839 *V*	1200		
35960 *W*	1000		
36064 *X*	600		
36153 *Y*	600		
36241°°	200		
36292	500		
36337	600		
36381	600		
36511	500		
36558	800		
36653	200		
36707			
36761			
36875			
36937			
37015			
37135			
37233	600		
37358			
37442			
37560			
37682			
37773	300		
37810			
37900			

° Indicates that the measurement is considered less reliable than the others. In most cases it comes from fewer than three plates but in others the overlapping of bands gives rise to the uncertainty.

°° From this point the bands tend to become diffuse.

‡ Values taken from Watson and Parker's tables.[7] Bands not observed or not sufficiently resolved for measurement on the present writer's plates. These fit in the proposed scheme as originating from excited vibrational states and so would show more prominently on plates taken at temperatures higher than have been used here.

[x] Value taken from Lotmar's[13] series. Not clearly resolved on the present writer's plates.

[L] The letters correspond to those identifying the peaks in the reproduced microphotometer trace.

The brackets embrace the bands considered in the various temperature variation groups. For each group the arbitrarily selected fiducial band is indicated ←. (See text). For bands to the higher frequency side of † no significant variation with temperature was found.

different initial levels. With any given tube length and pressure only a small group of bands out of the whole system appears favorably. Hence selecting an arbitrary band (*a*), the difference between the initial level of any other band (*b*) of the group and that of the selected band (*a*) is given by the relation:

$$\log_{10}(\rho_b/\rho_a) = -0.623(1/T_2-1/T_1)(G_b-G_a)'', \tag{1}$$

where the *G*'s are vibrational term values in cm^{-1} and ρ_b/ρ_a is the ratio on the traces of the heights of absorption peaks under examination above the line of zero absorption for the two temperatures.[12] The relation is valid only for small absorptions and a not overexposed continuous background.

As seen in Table I, temperature variation was considered in the five bracketed groups; for each group the arbitrarily selected fiducial band is indicated. To obtain reliable estimates of $(G_b-G_a)''$ it is important that the intensity range be not too great. The breaks between the groups are associated with somewhat sudden changes in the intensities, so that to relate the lower levels of the selected bands with overlapping spectrum photographs would require temperature variation comparison beyond the limits imposed in developing Eq. (1). Moreover very little confidence can be placed in the data obtained by comparing temperature variations of a band appearing at the end of one group and appearing at the beginning of the next. For in the first group the band appears with high and in the other with low intensity inasmuch as the exposure times for the two photographs are different.

For the group (4) just to the red of that showing no significant variation with temperature, the equation:

$$\log_{10}\rho_b = -0.623(1/T_2-1/T_1)G_b'' \tag{2}$$

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[13] W. Lotmar, Zeits. f. Physik **83**, 765 (1933).

was used to determine directly the term values G_b'' involved. This equation is developed in the same way as Eq. (1), except that the approximation $N_0^{(T_1)} = N_0^{(T_2)}$ is made for the small temperature change. Two of the stronger absorptions showed $G_b'' = 500$ cm^{-1}, so these were assigned as coming from $(0, 1, 0)''$.

An analysis of the band system must yield an arrangement in which the frequencies in the energy level diagram, the intensities of the transitions and the temperature behavior of the bands are consistent. The vibrational levels of the normal state are known to be spaced approximately according to multiples of 500 and 1100 cm^{-1}. If for a certain peak $(G_b - G_a)''$ comes out not a multiple of 500 or 1100 but as an intermediate value when an observed ρ_b/ρ_a is substituted in Eq. (1), it may be assigned to a suitable combination of overlapping components. For example, peak A (see microphotometer trace Fig. 1) gives $(G_b - G_a)''$ as 200 cm^{-1}, which has been interpreted (see Table III) as a not too close overlapping of transitions from $(0, 0, 0)''$, $(0, 3, 0)''$, and $(1, 0, 0)''$; further overlapping components are thought to be weak. When two bands, whose spectral frequencies suggest that they be assigned as coming from the same lower level, show a small difference in temperature behavior, it is assumed that one of them is composite and it is assigned a second time in the matrix diagram of bands in the place that this difference and the intensity seem to warrant.

THEORY

Any organization of the data must conform to the following theoretical demands.

(a) Group Theory[11]

The normal electronic state of this molecule of symmetry type C_{2v} may be safely assumed to be of type $^1A_1$, since SO_2 gas is diamagnetic. The excited electron state may then be A_1, B_1 or B_2, since only A_2 is forbidden to combine with A_1 according to electronic selection rules; however, weak transitions even to A_2 are possible if allowed by electronic × vibrational selection rules.[14] The normal modes of vibration ν_1, ν_2 and all resulting vibrational levels are of type a_1, while ν_3 is of type a_1 for v_3 even and b_2 for v_3 odd. The types of allowed transition will be summarized in tabular form taking the lower electronic state to be of type A_1. It will be noted that the capital letters refer to electronic types while the small letters are used to denote vibrational types. The absorption should be strong when both the electronic types and resultant electronic × vibration types are permitted by the group theory selection rules to combine. All selection rules developed will be strict even in the region of large vibrational quantum numbers, for the correction terms added to the representations of the vibrational motion to admit finite amplitudes must be of the same symmetry as those of the main term.

TABLE II. *Allowed transitions. Lower electronic state A_1.*

Upper electron state	v_3'' even		v_3'' odd	
	v_3'' even	v_3' odd	v_3' even	v_3' odd
A_1	z	y	y	z
A_2	—	(x)	(x)	—
B_1	x	—	—	x
B_2	y	z	z	y

The letter indicates the direction of vibration associated with the electric moment in the transition; z is the symmetry axis passing through the sulphur atom in the plane of the molecule, while x is the axis at right angles to this plane. The bracket indicates that the electronic change is forbidden.

If the configuration of the molecule in the normal state is an obtuse angled triangle,[3] the moments of inertia lie $I_x > I_z > I_y$, and remain in this order for apex angle 70–180°, so that the band structures should show differences for (y) and (z). An investigation of the rotational structure under high dispersion would be necessary to show the type of excited electronic state present.

(b)

In accordance with the Franck-Condon principle the two symmetrical frequencies would be expected to appear with greater or less intensity depending on the forms of ν_1 and ν_2 and the configuration of the molecule in the excited state. If the S–O force is approximately central in nature and the S–O distance does not change very greatly during the electronic transition, the value of ν_1' should be of the same order of magnitude as ν_1''. A series with frequency differences

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[14] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

very much less than this would then undoubtedly be a ν_2' progression.

Lower Frequency Bands

The temperature variation method points to a weak band at about 31,950 cm^{-1} as most probably the $(0, 0, 0)''-(0, 0, 0)'$ transition. However, other possibilities not convincingly ruled out on this score were tried as origin. The choice of 31,945 cm^{-1} gave a scheme so much more consistent and in accord with intensity and temperature behavior data that there can be little doubt of its correctness. Further, the fact that it fits in with a simple-appearing series of increasing intensity lends the assignment strong support.

On the basis of this assignment of origin, vibrational quantum numbers have been assigned for a large number of the prominent bands. These are given in the form of a matrix (Table III). The averages of the differences $\Delta G_2''$ between the v_2'' levels as taken from this table run 520 cm^{-1}, 525, 529, 530, 524, 522, 511, 526, 507 cm^{-1}, the latter two values appearing from only two

Table III. *Lower frequency bands.*

$(v_1v_2v_3)'$ / $(v_1v_2v_3)''$	000		010		020		030		040		050		060		070		080		090	Av.
000	31945	216	32161	216	32377	230	32607	243	32850	230	33088	225	33313	234	33547	213	33760	230	33990	
	518		515		519															518
010	31427	219	31646	212	31858		Masked by strong (ono)′ progression													
	532		522		528															527
020	30895*	229	31124	206	31330	237	31567	234	31801*											
	527		542		529		528		521											529
030	30368	214	30582	219	30801*	238	31029	241	31280	227	31507	212	31719	226	31945					
	534		534		539		539		539		537				518					534
040	29832	216	30048	219	30267	233	30500	241	30741	229	30970				31427					
	532		526		522		533				538				532					530
050	29300	222	39522	220	29742	225	29967				30432*	243	30675	220	30895*					
	498				519		521				536		536							522
060	28802*				29223	223	29446	246	29692	204	29896	243	30139							
	506						536				493		518							513
070	28296						28910				29403	218	29621*							
													526							526
080													29095							
													507							507
090													28588	230	28818	218	29036			
Av.		219		215		231		241		223		228		226		216		230		
100	30801*	227	31028	213	31241*				31707	219	31926	235	32161	216	32377	230	32607	243	32850	
	534		528		520						499		515		519					519
110	30267	233	30500	221	30721	240	30961				31427	219	31646	212	31858					
	525		533		536		529				532		522		498					525
120	29742	225	29967	218	30185	247	30432*	243	30675	220	30895*	229	31124	236	31360*	207	31567	200	31767	
	519		520		529		536		536		527		542							530
130	29223	224	29447	209	29656	240	29896	243	30139	229	30368	214	30582							
											546		506							526
140											29822	254	30076							
											522									522
150											29300									
Av.		227		215		242		243		223		230		221		218		221		
200	29621*	211	29832	216	30048	219	30267	233	30500	241	30741	229	30970							
			532		526		525		506				538							525
210			29300	222	29522	220	29742	252	29994				30432*				30855	210	31065	
			498						522				536							519
220	28588	214	28802						29472	220	29692	204	29896	207	30103					
			506												541					524
230			28296												29562	236	29798*			
															526					526
240	27510										28604	214	28818	218	29036					
	505												522							514
250	27005												28296	218	28514					
	536																			536
260	26469																			
Av.		213		219		220		242		230		216		214		236		210		
500	26253	216	26469	203	26672															
	520																			520
510	25733																			
	545																			545
520	25188																			
Grand Average		220		215		232		242		224		226		219		226		221		

Nine other observed frequencies have been fitted into the scheme in scattered places conforming with the general parabolic arrangement of intensity.

* indicates a value taken from Watson and Parker's data.[7]

pairs of bands. These may be summarized by the equation

$$G_2'' = 516.4v_2'' + 4v_2''^2 - 0.4v_2''^3.$$

The occurrence of series in which the ΔG's first increase, then decrease, is not unusual in polyatomic molecules.[9] For v_1'', the ΔG's obtained vary more widely, being 1144 cm^{-1}, 1195, 1157, 1111, 1102 cm^{-1}; they follow the formula

$$G_1'' = 1086v_1'' + 70v_1''^2 - 13v_1''^3.$$

The unsymmetrical frequency known in the normal state, $\nu_3'' = 1360$ cm^{-1}, has not been mentioned in the tabular analysis. Since the band system is of considerable intensity the possibility of the excited state being of type A_2 is excluded, and the ($v_3''=0$, $v_3'=0$) quantum jump should appear in the spectrum. Unless $\nu_3' \approx \nu_3''$, in which case $\Delta v_3 = 0$ is the most probable transition, transitions from excited unsymmetrical levels are to be expected among the lower frequency bands. The small frequency (see later) makes it probable that such bands are masked by overlapping; that is, if $(v_3'' - v_3')$ are approximately multiples of 225 cm^{-1}, the symmetrical and unsymmetrical progressions lie superposed. In an arrangement of the band system it would have been plausible to have assumed, for example, band 30,801 cm^{-1} as $(0, 0, 1)'' - (0, 0, 1)'$. However in view of the fact that the electronic type of the excited state, hence the selection rule for transition between unsymmetrical term values (see Table II), is unknown, any assignment in this way was felt would be purely arbitrary. The data for the vibrational levels of the normal state are collected in Table IV.

TABLE IV. *Vibrational levels of the normal state.*

	Level	Infrared[3]	Chow[15]	Lotmar[15]	Jonescu‡	Present writer
v_1''	0	0	0	0	0	0
	1	1152	1150 (A)	1150	(1144)	1144
	2		2300 (A)	2300	(2270)	2339
	3		3450	3450	(3378)	3496
	4		4600	4600	(4468)	4607
	5			5750	(5540)	5709
	6			6900		
v_2''	0	0	0	0	0	0
	1	525	521	520	(530)	520
	2		1043	1040	(1060)	1045
	3		1553 (A)	1560	(1590)	1574
	4		2069	2075	(2120)	2104
	5		2578	2590	(2560)	2638
	6		3086	3110	(3180)	3150
	7		3590	3630	(3710)	3661
	8		4093			
v_3''	0	0	0	0	0	0
	1	1361	1354?	1370	(1360)	
	2		2676?	2720	(2702)	
	3		3966?	4060	(4024)	

‡ Computed from the Deslandres' formulae given.

Table IV is of interest particularly with regard to the v_2'' series. Lotmar's values from fluorescence have very small second differences, and that the differences obtained by other workers show variation may perhaps be accounted for on the basis of band structure. It will be noted that Chow's emission values decrease with increasing quantum number, while the values in absorption run larger. That is, in emission we must say that the point of maximum intensity in the rotation band is distant from its origin by an amount which varies from band to band. In absorption the point of maximum absorption should also vary, only in this case the variation might be in the opposite direction.

HIGHER FREQUENCY BANDS

While the bands on the lower frequency side of the origin fall into the matrices shown in Table III, those on the higher frequency side, with the exception of the first eight members, present a confused and irregular appearance (see Fig. 1—sample microphotometer trace). Since the frequencies cannot be made to follow regular progressions, partly because the values are taken for the points of maximum absorption in each band, but perhaps mainly because of some inherent disturbances in the levels of the upper state, the microphotometer trace was examined for clues to an organization. It will be seen in Fig. 1 that the intensity increases to peak G, then follows a plateau of intense peaks, after which comes a somewhat regular decrease of intensity in the neighborhood of V. Finally appears a region of collision predissociation about 2600A, which has been explained as pressure broadening due to an influence of the existence of neighboring electron states.[16] This predissociation occurs only when selection rules are broken down by collision. The perturbing influence of the discrete levels of these same, or other, states may perhaps

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[15] The summary of Chow and Lotmar's values is taken from H. D. Smyth, Phys. Rev. **44**, 690 (1933).

[16] J. Franck, H. Sponer and E. Teller, Zeits. f. physik. Chemie **B18**, 88 (1932).

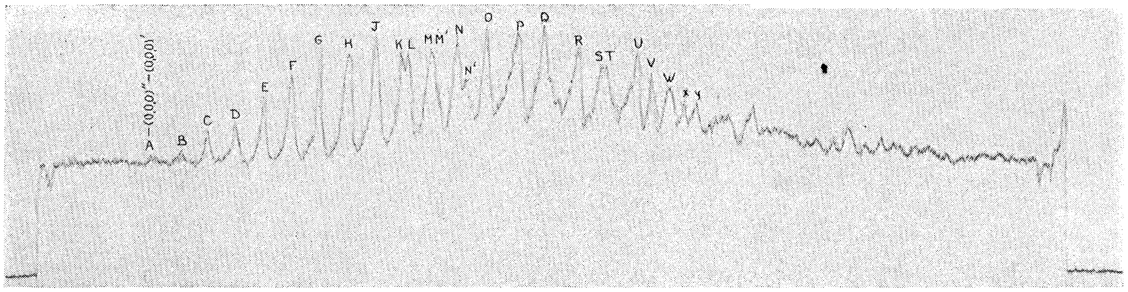

FIG. 1. Microphotometer trace of higher frequency bands. (Many lower frequency bands appear to the left of (0, 0, 0)''$-$(0, 0, 0)' with larger numbers of molecules in the absorption path.)

be invoked to explain the irregularities among the lower frequency bands.

The plateau of intensity suggests the overlapping of a number of series of about equal intensities. In looking for the beginning of the $(1, v_2, 0)'$ progression the double peak *KL* is first arresting; but that the doubling indicates the first member of this progression is little likely in that the frequency interval, 2045 cm^{-1}, is somewhat larger than expected. Also the unsymmetrical appearance of peak *H* argues that the new series begins at lower frequency. Particularly striking also is the intense band *O* which is apparently rather free of satellite peaks. The appearance of the fairly intense peak *V*, obviously in a new series without distinct previous members, is also interesting. These observations have led to the placing of the beginning of the new progression at *G* (see Table V).

As in the series beginning with *A*, the intensity may be assumed to rise slowly, *G* being affected negligibly, *H* and *J* with increasing influence with the maximum of intensity at the sixth member *O*, corresponding to the most intense sixth member *G* in the $(0, v_2, 0)'$ sequence. If this has been correctly placed, the $(2, v_2, 0)'$ progression begins with *O* and the $(3, v_2, 0)'$ progression with *V*. The v_1' levels on this analysis converge rapidly and there is obviously some disturbance in the spectrum at peak *O* (indicated by the line drawn in Table V), which, however, is to be expected in any organization in view of the different appearance of satellites in the bands on the two sides of *O*. Perhaps this is due to an interaction of the normal modes of vibration in the upper states, and since ν_1, ν_2 and even multiples of ν_3 belong to the same representation of the symmetry group, such an interaction is not improbable. If this is the case, the scheme drawn up is simply an attempt to approximately separate ν_1' and ν_2'. With increasing amplitudes of vibration of the molecule corresponding to the higher vibrational quantum numbers, the interaction may be supposed to increase, and that a sudden increase in coupling might occur in the upper state corresponding to the energy $A-O$, should not be regarded as too strange.

The apparent disturbance at *O* in Table V may be explained perhaps more satisfactorily on the basis of a sharp decrease of intensity in the $(1, v_2, 0)'$ progression at $v_2'=6$. Such intensity irregularities are known in the spectra of diatomic molecules.[17] If this is the case here, the bands

TABLE V. *Proposed transitions from (0,0,0)''.*

	$(0,v_2,0)'$		$(1,v_2,0)'$		$(2,v_2,0)'$		$(3,v_2,0)'$
$v_2'=0$	*A* 31945	1368	*G* 33313	1307	*O* 34620	1219	*V* 35839
	216		217		226		225
1	*B* 32161	1369	*H* 33530	1316	*P* 34846	1218	*X* 36064
	216		230		207		228
2	*C* 32377	1383	*J* 33760	1293	*Q* 35053	1239	36292
	230		235		244		219
3	*D* 32607	1388	*KL* 33995	1302	*R* 35297	1214	36511
	243		220		198		196
4	*E* 32850	1365	*MM'* 34215	1280	*ST* 35495	1212	36707
	230		225		247		230
5	*F* 33080	1360	*NN'* 34440	1302	*V* 35742	1195	36937
	233		180		218		198
6	*G* 33313	1307	*O* 34620	1340	*W* 35960	1175	37135
	234		226		198		223
7	*H* 33547	1299	*P* 34846	1307	*Y* 36158	1200	37358
	213		207		223		202
8	*J* 33760	1293	*Q* 35053	1328	36381	1179	37560
	235		244				
9	*KL* 33995	1302	*R* 35297				
	220		198				
10	*MM'* 34215	1280	*ST* 35495				
	247		247				
11	*NN'* 34462	1280	*V* 35742				
	236		218				
12	34698	1262	*W* 35960				

In this table $\Delta v_2'$ differences are shown horizontally and the $\Delta v_1'$ differences vertically. The break in the frequency differences at *O* is discussed in the text.

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[17] For example, R. W. Wood and F. W. Loomis, Phil. Mag. **6**, 231 (1928); I_2 fluorescence. R. S. Mulliken, Phys. Rev. **25**, 259 (1925); BO.

below the line in $(1, v_2, 0)'$ are wrongly assigned, and since peak O is without a strong satellite where $(1, 6, 0)'$ should appear, the bands O, P, Q, should be placed as belonging to the $(2, v_2, 0)'$ progression alone. That this is the more plausible assignment is substantiated by the fact that peak V, $(3, 0, 0)'$, is much the strongest member of the $(3, v_2, 0)'$ progression, and thus the $(2, v_2, 0)'$ progression may well have a first member with relatively high transition probability.

The first few v_2' levels should in any case not be of mixed type and their intervals appear in Table III. These levels may be represented by the formula

$$G_2' = 219v_2' + 1.0v_2'^2 + 0.5v_2'^3,$$

which however fails to take into account the small decrease in the difference between the second and third levels. The v_2' frequency difference, approximately 225 cm^{-1}, as already noted by Lowater[18] is prominent throughout the band system. The v_1' levels, if the assignment of bands just given is correct, may be approximately summarized

$$G_1' = 1373v_1'^2 - 7v_1'^2 - 6v_1'^3.$$

No bands corresponding to transitions from excited vibrational levels of the normal state to levels of the excited state involving v_1' greater then zero have been assigned. In view of the coincidence $\nu_3'' = \nu_1'' + \nu_2'$ and the approximate coincidences $\nu_3'' \approx 6\nu_2'$, $\nu_1'' \approx 5\nu_2'$, together with the uncertainties in the frequencies due to overlapping, such a definite assignment of satellite peaks does not seem justified. No significant temperature variation of these satellite peaks has been observed; this would indicate that these are weak if this interpretation of them is correct. $(1, 0, 0)'' - (1, v_2, 0)'$ might show most favorably through temperature changes among the weaker bands near the origin, but it is believed that the transition probability of these in this region is small.

The double bands KL, MM' and ST with reduced intensity as compared with adjoining peaks are of interest. The doubling may be ascribed to a resonance splitting of the level due to another level in close proximity, in which case the intensity of transition would be shared. Against this assumption is the apparent absence of splitting in the neighboring levels which should also be favorably placed to show the effect. Another peculiar feature of the spectrum is the slight alternation of intensity shown in the bands A−J. This at first suggested two progressions, but if so, the two progressions could not converge to the same point. No reasonable explanation of the phenomenon has been found.

CONFIGURATIONS AND FORCE CONSTANTS OF THE SO_2 MOLECULE

From infrared investigations Bailey and Cassie[19] conclude that the normal apex angle is 122° although their valence force assumption permits both a 60° and a 120° solution. This conclusion rests on the identification of the 1360 cm^{-1} frequency as the unsymmetrical one. In the analogous molecule, ClO_2, Ku[10] on the other hand favors the acute angled form.

Van Vleck and Cross[20] have developed a valence force solution for this type of molecule, which on a present calculation leads to values of the force constants $(S-O) = 9.8\ 10^5$ and $(O-O) = 0.42\ 10^5$ dynes/cm. Here the cross terms in the potential energy expression are neglected, although if the $(O-O)$ force is partly central in character for SO_2 these may be of importance. However a purely central force assumption does not give a solution for the frequencies observed. The $S-O$ distance used in the present calculation is that obtained by Wierl[21] from electron diffraction, *viz.*, 1.37A. From crystal structure data the $S-O$ distance corresponding to a single bond should be about 1.50A, while that corresponding to a double bond should be about 1.35A. If one of the bonds is single and the other double the resultant value should be closer to the double bond distance due to the exchange energy.*

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[18] F. Lowater, Astrophys. J. **31**, 311 (1910).

[19] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London **A140**, 605 (1932).

[20] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

[21] W. Wierl, Phys. Zeits. **31**, 1028 (1930).

* My thanks are due to Professor Zachariasen of this department for a discussion on this point. In his opinion also the apex angle should not be greatly different from the tetrahedral angle 125°.

If the molecule is in the normal state when it absorbs the incident light, then the transition will be strongest to the excited state for which the end-point of the vibrational motion (i.e., all the vibrational energy potential) puts the molecule in the configuration most nearly that of the normal state. The intensities in Fig. 1 and the proposed arrangement in Table V show there is no single band that may be definitely taken to be the most probable transition from $(0, 0, 0)''$. The probabilities of transition of $(v_1''-v_1')$ and $(v_2''-v_2')$ (to the extent that these may be considered unmixed ν_1 and ν_2 in the two electronic states) in combination cause a number of bands to appear with about the same intensity. If the intensity explanation of the disturbance at peak *O* is accepted, a parabola of maximum intensities can be drawn in Table V. Selecting a central value on this parabola, the excited molecule vibrating with $v_1'=1$, $v_2'=3$, $v_3'=0$ may be taken as having vibrational energy potential sufficient to put the molecule in the configuration of the vibrationless normal state. The energy difference $(1, 3, 0)'-(0, 0, 0)'$ is 2050 cm^{-1} (0.25 volt). Since the S$-$O distance and the OSO angle both undoubtedly change from their values in the normal electronic state, it is not possible from this data to determine the shape and dimensions of the molecule in the excited state.

Jonescu[22] from a partial rotational analysis reports the OSO angle in the excited state as 96°. With the frequencies 225 cm^{-1} and 1370 cm^{-1} recognized in the spectrum, Eq. (4) of Bailey and Cassie[23] was used to suggest a possible ν_3' frequency. The solutions are in the neighborhood of 1400 and 250 cm^{-1}; the former involving the less change from the unsymmetrical frequency in the normal state appears the more likely. If then the unsymmetrical frequencies in the two states are so nearly equal it is not surprising (see discussion earlier) that these were not identified in the spectrum.

The writer wishes to thank Professor R. S. Mulliken for the suggestion of the problem and for much help and encouragement throughout the investigation.

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[22] A. Jonescu, Comptes rendus **196**, 1476 (1933).

[23] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London **A137**, 630 (1932).

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The Spectra of Lead IV and Bismuth V

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Early investigations in the spectra of Pb IV by Rao and Narayan, Smith and Kishen have been extended to include 34 terms arising from the configurations $5d^{10}ns$, $5d^{10}np$, $5d^{10}nd$, $5d^{10}5f$, $5d^96s^2$, $5d^96s6p$ and $5d^96s6d$. With data by Arvidsson, Smith and the author, the region reported extends from 198 to 5005A and 79 lines have been classified. In the extension to Bi V, values have been assigned to 14 terms involving 18 lines in the region below 1487A. By a Hick's formula the value of the $5d^{10}6s\ {}^2S_{0\frac{1}{2}}$ term has been computed to be 340,885 cm^{-1} for Pb IV and 451,700 cm^{-1} for Bi V, giving ionization potentials of 42.0 and 55.7 volts, respectively.

PREVIOUS investigations of Pb IV by Rao and Narayan,[1] and Smith[2] established terms arising from the configurations $5d^{10}6s$, $5d^{10}6p$, $5d^{10}7s$, $5d^{10}7p$, $5d^{10}6s$, and $5d^{10}7d$ with optional assignments for the last four configurations, these assignments being commented upon by Kishen[3] in a brief note to *Nature*. Arvidsson[4] measured the spectrum below 1440A due to transitions in the various states of ionization of Pb and accordingly classified the lines as to their states of ionization. Using these data and the measurements by Smith[5] for the region 2200 to 5005A and measurements by the author for the inter-

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[1] Rao and Narayan, Zeits. f. Physik **61**, 151 (1930).

[2] Smith, Phys. Rev. **36**, 1 (1930).

[3] Kishen, Nature **130**, 739 (1932).

[4] Arvidsson, Ann. d. Physik **12**, 1 (1932).

[5] Smith, Trans. Roy. Soc. Canada **22**, 331 (1928).

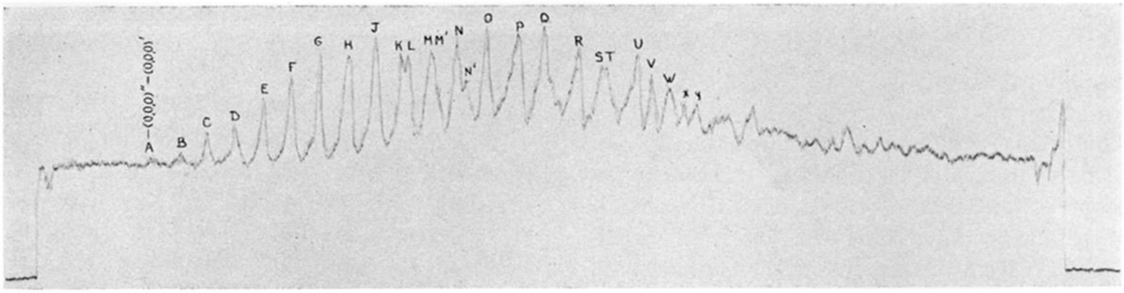

FIG. 1. Microphotometer trace of higher frequency bands. (Many lower frequency bands appear to the left of (0, 0, 0)'' − (0, 0, 0)' with larger numbers of molecules in the absorption path.)