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The Spectrum of Sulphur Dioxide

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A study has been made of the emission and absorption spectrum of sulphur dioxide with special emphasis on the region from 2000 to 2600A. It was found possible to run a discharge in flowing SO_2 with comparatively little dissociation. The work on absorption was supplementary to that on emission and carried out at the same moderate dispersion. A large proportion of both the emission and absorption bands found fit into a scheme of vibrational levels. The upper levels indicate a frequency of about 375 cm^{-1} or an integral multiple of that value. The lower levels confirm the 1150 and 520 frequencies previously observed but leave the third frequency in doubt. The $x_e\omega_e$ for both the 1150 and 520 frequencies are small, of the order of one cm^{-1} for the latter as determined from a progression of sixteen bands.

Two years ago a systematic study of emission spectra of polyatomic gases was begun in this laboratory by Smyth's[1] work on carbon dioxide. The present author undertook a similar study of sulphur dioxide but found it desirable to extend his original plan to include the investigation of the absorption spectrum as well as the emission spectrum.

There was already a good deal of information available about the spectrum of sulphur dioxide. The absorption spectrum had been first studied in the region between λ3882 and λ2200 by Miss Lowater.[2] Henri[3] later reported three systems of absorption bands; one weak system from 3900A to 3400, one moderately strong system from 3370 to 2450 and one very strong system from 2350 to 2000 and beyond. There was no evidence that these systems corresponded to three electronic transitions except the fact that the three portions were greatly different in absorbing power. Watson and Parker[4] measured the bands in the region from λ3880 to 2630. They picked out bands (about 20 percent of the total) from this region and arranged them into progressions, using the fundamental frequencies 1369 (ν_3), 1164 (ν_1) and 610 (ν_2) cm^{-1} for the lower state and 341, 387 and 290 for the excited state. In view of the new interpretation of the infrared spectrum the 610 cm^{-1} frequency is probably incorrect. Nor do the frequencies of the upper state seem probable.

The study of the emission spectrum was also started by Lowater.[2] Later studies made by Johnson and Cameron,[5] by Henri and Wolff,[6] by Martin[7] and by Bair[8] show two different spectra. The one most easily obtained and most extensively studied is definitely attributable to SO. Another set of bands, degraded toward the violet were found by Johnson and Cameron, and by Bair. These are apparently from SO_2 and in fact can be very simply correlated with some of Watson and Parker's absorption bands as was pointed out by Chow and Smyth.[9] Other bands were found by Bair scattered over the region between 2200 and 3200A and for the most part degraded toward the red.

In the present work measurements of the SO_2 bands, particularly those of shorter wave-length, have been repeated and extended both in emission and absorption. An attempt has then been made to arrange the observed wave-numbers in a rational scheme of vibrational levels.

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[1] H. D. Smyth, Phys. Rev. **38**, 2000 (1931) and the literature given there.

[2] F. Lowater, Astrophys. J. **23**, 324, 338 (1906); **31**, 311 (1910).

[3] V. Henri, Nature **125**, 275 (1930).

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

[5] R. C. Johnson and W. H. B. Cameron, Proc. Roy. Soc. **A106**, 195 (1924).

[6] V. Henri and F. Wolff, J. de Physique et le Radium **10**, 81 (1921).

[7] Emmett V. Martin, Phys. Rev. **41**, 167 (1932).

[8] Bair, Astrophys. J. **52**, 301 (1920).

[9] T. C. Chow and H. D. Smyth, Phys. Rev. **38**, 838 (L) (1931).

Experimental

The first thing attempted was the reproduction of the emission bands observed by Johnson and Cameron between 3105 and 2866A. This was unsuccessful but a great number of bands was observed below 2300 and attention was directed to them.

For studying polyatomic spectra the first essential is a constant flow of gas. In the present experiment, sulphur dioxide was let into the discharge tube from the reservoir through an artificial leak and was drawn out by condensing it in a liquid-air cooled trap on the other side of the discharge tube. A three-stage Gaede diffusion pump was also operating to take care of the oxygen resulting from dissociation in the discharge tube. The amount of dissociation and loss of SO_2 resulting from passage through the discharge was found to be less than 4 percent. The sulphur dioxide was from an ordinary tank of SO_2 but was distilled under vacuum several times before use and was stored over P_2O_5.

After trying a number of types of discharge it was concluded that a weak glow discharge in a tube, such as is shown in Fig. 1, was most suitable. This was run at a pressure of about 0.5 mm with a voltage of 920–1100 and a current of 3 to 5 m.a. When such a discharge was running properly there was no sulphur deposit detectable on any part of the walls of the tube after a run of twenty hours. It was the positive column that was photographed. This filled the whole narrow glass tube with a bluish violet color. The quartz window was put as near as possible to the source to avoid reabsorption.

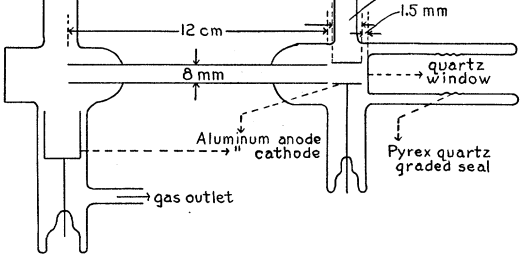

FIG. 1. Discharge tube.

The source proved too weak to give satisfactory plates with a Hilger E 1 spectrograph and consequently all our measurements are from plates taken with the medium size quartz Hilger, E 315. The spectra on these plates can be generally described as consisting of the SO bands (4000–2500A) studied by Henri and Wolff[6] and by Martin,[7] and a set of bands of entirely different character in the region 2600–2040A (38,000–49,000 cm^{-1}). Fortunately the main parts of the two sets do not overlap. The measurements of band heads and of some of the maxima of the bands (where the heads were not sharp) are assembled in the table below. The discussion of these bands will be given later.

The Absorption Spectrum

In this short wave-length region the only absorption measurements available were by Garret[10] and were not sufficiently accurate to compare with our emission data. Therefore a study of the absorption spectrum was made. The continuous spectrum of a hydrogen discharge was sent through an absorption cell 23.5 cm long filled with SO_2 at a pressure of from 0.08 to 10 mm. This was at room temperature. Some plates were also taken at 240°C with a 7.8 cm quartz tube in an electric furnace as an absorption cell. The band heads observed are listed in Table I. A more thorough study of the absorption spectrum by using a bigger instrument was not carried out mainly because it was known that two other investigators were working on this problem. However, the plates obtained were very useful for comparison with those showing emission. In each case various checks led to the conclusion that the accuracy of the measurements is about 5 cm^{-1} or better.

Before attempting an analysis of the emission bands it is necessary to establish their origin. They might conceivably arise from SO_2, SO, SO^+, O_2, O_2^+, S_2 or S_2^+. Each of these possibilities has been considered in detail and all but the first discarded as unlikely. The strongest evidence for the assignment of the bands to SO_2 is the absence of fine structure (at the dispersion used) and the many coincidences between the emission and absorption wave numbers. It is believed safe to

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[10] Scott Garret, Phil. Mag. **31**, 505 (1906).

TABLE I. *Emission and absorption bands in sulphur dioxide.*

Absorption	Transition	Emission	Transition
50302	A_6		
50248	C_5		
49910	B_5		
49550	A_5		
49477	C_4		
49133	B_4		
48781	A_4	48789	A_4
48724	C_3		
48375	B_3	48387	B_3?
		48269	b_1A_4
48355	b_3B_5		
48121			
48083			
48005	A_3	48009	A_3
48000	b_3A_5		
47965	C_2		
47922	b_3C_4		
47889	α_1A_5		
		47776	
47742		47747	b_2A_4
47707	α_2B_5		
47636	a_1A_4	47631	B_2?, a_1A_4
47623	B_2		
47576	a_1C_3, b_3B_4	47586	b_3B_4
47548			
		47489	b_1A_3, b_4A_5
47391			
		47345	α_2A_5
47246	A_2, a_2A_5		
47232	a_1B_3	47230	A_2?, a_1B_3, b_3A_4
47223	C_1, a_1B_3, b_3A_4		
47198			
		47110	b_1B_2, α_1A_4
47074			
47052	α_1C_3		
		47031	
		46968	b_2A_3, b_5A_5
46874	B_1	46871	B_1
46865	a_1A_3	46851	a_1A_3, a_3A_6
46829	a_2B_4		
46818	a_1C_2, b_3B_3		
46704	α_1B_3	46710	b_4A_4, α_1B_3
46697			
		46632	δ_1B_4
		46588	b_2B_2, α_2A_4
46570			
46482	C_0, a_2A_4		
46472	a_1B_2	46474	a_1B_2, a_2A_4, b_6A_5
46464			
46444	b_3A_3		
		46425	
46348		46350	b_1B_1
		46330	b_7B_5
		46277	δ_1A_4
		46259	
46217			
		46190	b_2A_2?
46118	B_0		
46104	a_1A_2	46105	a_1A_2, a_3A_5
46084		46094	
46077	a_1C_1, a_2B_3, b_3B_2	46074	a_2B_3, b_3B_2
		46060	
		45968	b_7A_5
45923			
		45888	
45859			
		45833	b_2B_1
		45817	b_8B_5
45757	A_0, α_2C_2	45757	A_0
45725	a_1B_1	45717	a_1B_1, a_4A_6
45706	a_2A_3		
45686	b_3A_2		
45672	a_2C_2, b_3C_1	45665	
		45588	b_1B_0, α_1A_2
45572		45560	b_4B_2
		45500	δ_1A_3
		45455	b_2A_1, b_8A_5
		45414	α_2B_2
45393			
		45367	
45351	a_1A_1	45350	a_1A_1
45333	a_1C_0, a_2B_2		
		45314	b_3B_1, b_9B_5
		45199	α_1B_1
		45188	
		45119	δ_1B_2
		45069	b_2B_0
		45051	b_5B_2
45030	α_2A_2		
44987			
44978	a_1B_0	44977	a_1B_0
		44953	a_2A_2, b_9A_5
		44833	α_1A_1
		44798	b_4B_1
44674		44672	α_2B_1
44663	α_2B_1		
44603	a_1A_0		
44570	a_2B_1, b_3B_0	44573	a_2B_1, b_3B_0
		44543	b_6B_2, a_4B_4
		44457	$b_{10}A_5$
		44437	b_4A_1
		44362	δ_1B_1
		44340	
44305		44310	$b_{11}B_5$
44293	α_2A_1	44285	α_2A_1
44236			
		44199	a_2A_1, b_3A_0
		44121	
44100			
44085			
		44057	b_4B_0
		44039	b_7B_2
43929		43925	b_5A_1
43918	α_2B_0		
		43824	
		43807	a_2B_0?, a_3A_2, $b_{12}B_5$
43714			
		43683	b_4A_0, γ_1B_2
		43657	
43550	α_2A_0		
43538			
		43453	a_2A_0, $b_{11}A_5$
43407		43406	b_6A_1, a_4A_3
43340			
43329			
		43310	$b_{13}B_5$, γ_3A_2
43145		43140	
43137			
		43054	a_3A_1
		43034	b_6B_0
43018			
42966			
42954			
		42938	γ_1B_1
		42895	b_7A_1?
		42847	
42759			
		42681	
		42658	a_3B_0, a_4A_2
		42634	
42589			
42575			

TABLE I. (*Continued.*)

Emission	Transition	Emission	Transition	Emission	Transition	Emission	Transition
42531	b_7B_0	41600		40735		39412	$b_{14}A_1$
42525	$b_{10}B_2$	41573		40644		39372	
42513		41544		40598		39351	
42366	γ_2B_2	41530	b_9B_0, $b_{12}B_2$	40534		39335	
42306	a_3A_0, $b_{15}B_5$	41422		40522	$b_{11}B_0$, $b_{14}B_2$	39224*	
42271	a_4B_1	41398	$b_{10}A_1$	40482		39137*	
42251		41380		40372		39087	
42171	γ_1B_0	41346		40330	$b_{19}B_5$	39074	
42156		41313	$b_{17}B_5$	40278		39061	
42103		41231		40139		38977	γ_4B_1
42079		41108		40100		38956	
41994	γ_2A_2	41089		40008	$b_{12}B_0$	38919	
41923		41038	$b_{13}B_2$, γ_3B_2	39973		38907	$b_{15}A_1$
41902	b_9A_1	41022	$b_{10}B_0$	39930		38847	
41855		40939		39855*		38723*	
41817	$b_{16}B_5$	40888		39825		38611*	
41802		40859	γ_2B_0	39755		38534	
41723		40841		39730		38232	
41701		40822	$b_{18}B_5$	39541	$b_{16}B_2$	38213	
41661		40767		39522	$b_{13}B_0$		
41621	γ_2B_1	40743		39472			

* SO band.

conclude that the bands under consideration arise from the sulphur dioxide molecule both in emission and absorption.

The wave numbers given in Table I are in most cases the violet edge of bands degrading toward the red. In the cases of a few very diffuse bands the measurements are of intensity maxima. The first column gives the wave numbers measured in absorption, the third those in emission. The second and fourth columns give the suggested transitions in terms of the levels of the upper and lower states shown in Fig. 3. These transitions are recorded only where the agreement between observed and calculated values is better than 10 cm^{-1}. Nor are transitions recorded where the agreement is good but the absence of other bands in the progression indicates that it is accidental. The levels used are discussed below.

ANALYSIS OF ABSORPTION DATA

The most striking features of the absorption spectrum are seen more clearly in the densitometer records of the plates than in the plates themselves. Such a record is reproduced in Fig. 2. The most natural assumption seems to be that the strong bands or groups of bands standing out so clearly on the short wave-length side of the spectrum correspond to transitions from the normal state of the molecule to various vibrational states of an excited electronic level. There are nine or ten of these groups with separations of about 370 cm^{-1}. Closer inspection shows that

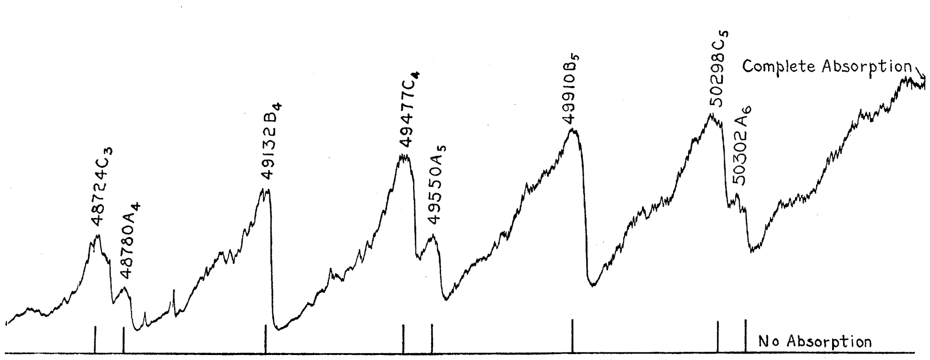

FIG. 2. Densitometer record of part of plate showing absorption spectrum of SO_2 at a temperature of 240°C, pressure of 1.5 mm and path length of 7.8 cm.

these groups do not constitute a simple v' progression as both their structures and separations vary in a complicated way. Various level schemes give a fairly satisfactory correlation of the band heads but none has been found that seems so much better than the others as to be established with certainty as the correct one. In any case the various level schemes devised have certain features in common. For the upper levels the vibrational frequencies used are of the order of 375 cm^{-1} or integral multiples of that number. The separation of successive levels seems to increase for the first two or three and then to decrease again. This effect can be seen clearly in the upper level scheme of Fig. 3 which is the most satisfactory on the whole. On this scheme one vibration frequency is about 750 to 770 cm^{-1} with the others uncertain, though the constant differences $B_n - A_{n-1} = 1129$ suggest this as another. An interesting point is the regular increase of the A_nC_{n-1} separation, the successive values being 23, 40, 57, 73 and 54 cm^{-1} giving a second difference of 17 cm^{-1} if the last value be omitted. However the C levels are necessary for only a few bands and most of their combinations with the lower levels are definitely missing or coincide with other bands. They are perhaps not real.

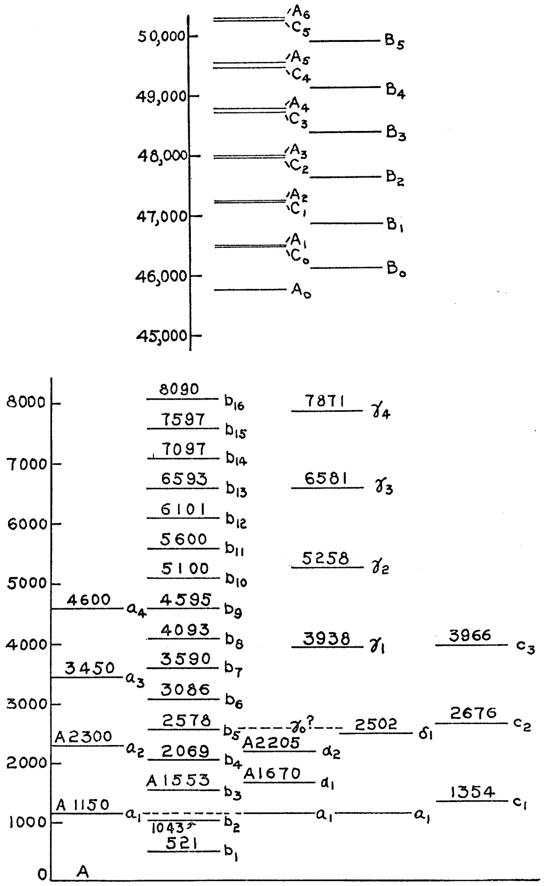

FIG. 3. Vibrational levels in SO_2. In upper electronic state C levels were not used in analyzing emission spectrum. In lower (normal) electronic state only levels marked A were used in analyzing absorption spectrum.

A single lower level and the triple system of upper levels given in Fig. 3 explain the principle features of the strong absorption shown in the densitometer record. But if this record is examined more carefully or the table of measured wave-lengths consulted it is clear that there are many bands that do not fit into such a scheme. Probably there are many more vibration levels in the upper state than have been used but it is also probable that other levels than that of zero vibration in the normal state contribute to the absorption. From the Raman[11] and infrared[12,13] spectra we know that the vibration frequencies of the normal state are $\nu_1 = 1150$, $\nu_2 = 525$ and $\nu_3 = 1360$ (or 1340?). An examination of the measurements shows 1150 cm^{-1} differences frequent but 525 and 1360 differences only occasional. Levels corresponding to $v_1'' = 1$ and 2 at 1150 and 2300 are well established and combination levels at 1674 for $v_1'' = 1$, $v_2'' = 1$ and at 2210 for $v_1'' = 1$, $v_2'' = 2$ seem probable. A level at 1555 $v_2'' = 3$ also gives several bands and is included in spite of the absence of $v_2'' = 1$ and 2.

The intensities of the bands from the higher vibrational states are lower than those from the initial state as they should be, but there is no consistent variation with temperature between the plates taken at room temperature and 240°. However these experiments were not sufficiently extensive to be of much value.

The predominance of vibrations involving ν_1 in the lower state remains unexplained, particularly as ν_2 and perhaps ν_3 states were observed in emission. It suggests the possibility that the observed 1150 differences should be attributed to

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[11] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London, **A137**, 622 (1932); C. R. Bailey, A. B. D. Cassie and W. R. Angus, Proc. Roy. Soc. London, **A130**, 142 (1930).

[12] K. W. F. Kohlrausch, *The Smekel-Raman Effect*, p. 172.

[13] Dadieu and Kohlrausch, Phys. Zeits. **33**, 165 (1932).

the upper state, the 1128 difference already observed there being the interval between the second and third levels of this particular vibration.

Analysis of Emission Data

Taking the same upper levels and lower frequencies used for absorption it is possible to put some 70 percent of the emission bands into a level scheme. As is to be expected many new levels appear in the lower state. These are shown in Fig. 3. The most striking features are long v_2'' progressions. In one case there are transitions from the B_2 upper level to 17 ν_2'' levels having successive differences between 520 and 493 cm^{-1}. Other v_2'' progressions are interpreted as transitions from B_0, A_1, A_5 and B_5 to the same set of lower levels.

The $v_1''=1$, 2 levels appear as in absorption. A level at $v_1''=3$ gives a number of bands but most of them correspond to other transitions also. The $v_1''=4$ level falls on the $v_2''=9$ level.

A search was made for v_3'' progressions and the levels c_1, c_2, c_3, were established tentatively as $v_3''=1$, 2, 3. The same differences among bands of lower wave number led to the γ_1, γ_2, γ_3 levels interpreted as $v_2''=5$, $v_3''=1$, 2, 3. However, all but one of the bands given by the c levels have other interpretations so that no c transitions are recorded in the table. This is not the case with the γ levels but their interpretation is very dubious.

Turning to other combinations, transitions to the α_1, α_2, i.e., $v_1''=1$, $v_2''=1$, 2 levels of absorption are also present in emission. An additional level $\delta_1=2502$ is quite well established and is apparently $\nu_1+\nu_3$.

It may be of interest to note that the second differences in both the v_1'' and v_2'' progressions are very small. A similar result has been observed in CO_2.

Fluorescence

Just as the number of lower levels involved is restricted in an absorption spectrum the number of upper levels observed is restricted in a fluorescence spectrum. Mr. Lotmar in Göttingen has kindly communicated to us his preliminary results on fluorescence in SO_2. They seem to be reconcilable with the level scheme suggested above but not an emphatic confirmation of it. A detailed discussion must await publication of Lotmar's work.[14]

The Electronic States of SO_2

In the early part of this paper the possibility was mentioned that there was more than one electronic transition involved in these spectra. The present work deals mainly with the shortest wave-length portion of the spectrum. Absorption here is stronger than that at longer wave-length and is separated from it by a gap. Furthermore no emission bands were found on our plates above 2600A. It seems probable that there are two excited states, one having a ν_e of about 46,000 and the other having a ν_e of about that used by Watson and Parker, i.e., 31,500 cm^{-1}. The publication of the data on fluorescence may throw further light on the question.

The ultimate purpose of the experiments described in this paper was to throw light on the structure of SO_2 molecule in normal and excited states, its normal vibrations, translation probabilities, etc. But the results seem hardly to justify a discussion of these questions as yet. It is hoped, however, that they may be of assistance to others working in this field.

In conclusion the writer wishes to express his deep gratitude to Professor H. D. Smyth who directed this work and helped to prepare this article. He also wants to thank Professor R. Ladenburg and Professor A. G. Shenstone for their help.

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[14] *Note added in proof:* Lotmar's paper appeared in the Zeits. f. Physik **83**, 765 (1933) and is discussed in a letter by Smyth in this issue of the Physical Review.