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Vibrational Analysis of the Absorption System of Sulphur Dioxide at λ3400–2600

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Photographs of the bands of sulphur dioxide in the region of λ3400–2600 have been taken under low, medium and high dispersion, both at room temperature and at 200°K; the pressure of the absorbing gas was varied from 0.3 mm to 480 mm. Thirty bands can be represented by the formula

$$\nu = 29622 + 770v'_1 + 320v'_2 + 813v'_3 - 6v'^2_1 - 2.5v'^2_2 - 20v'_1v'_2 - 25v'_2v'_3 - 15v'_1v'_3,$$

where v'_1, v'_2, v'_3, are the quantum numbers of the symmetrical valence, the deformation and the antisymmetrical vibrations respectively. The three fundamental frequencies for infinitesimal vibrations in the upper electronic state are $\nu'_1 = 794$, $\nu'_2 = 345$ and $\nu'_3 = 833$ cm^{-1}. In addition, twelve bands have been identified that correspond to transitions from excited vibrational levels in the normal state. The relatively long v'_1 and v'_2 progressions indicate that both the bond distance and the angle have changed considerably in the transition to the excited electronic state. The vibrationless transition at 29622 cm^{-1} is weak, as one would have expected from considerations of the Franck-Condon principle. Substituting the three fundamental frequencies in the formula based on a valence force model, one obtains a value of 100° for the apex angle in the excited state, as compared with 120° in the normal state. The absence of any regularity in the rotational structure supports the resulting conclusion that the molecule in its upper state has become a more asymmetrical top.

INTRODUCTION

THE vibrational structure of the absorption bands of sulphur dioxide in the region λ3900–2600 has been studied in recent years by several investigators.[1–5] Previously Henri[6] had reported three main absorption regions in the near ultraviolet, (1) λ3900–3400, weak; (2) λ3370–2450, moderately strong; (3) λ2300–2000 and beyond, very strong. There was no evidence that these absorbing regions corresponded to three different electronic transitions except that the absorption intensities varied so widely. Watson and Parker[2] and Clements[4] investigated the absorption in regions (1) and (2) and concluded that both regions constitute one system; the bands at longer wave-lengths (λ3900–3400) were considered as transitions from excited vibrational states of the normal electronic state. Clements identified a moderately strong band at 31945 cm^{-1} as the band origin.

Retaining the assumption of a single upper electronic state, Samuel and Asundi[5] proposed two alternative analyses, the first a modification of the analysis of Clements, the second entirely new, with the vibrationless transition at 33303 cm^{-1}, one of the most intense bands. However, the proposals of Samuel and Asundi are not free from objections, as they themselves have remarked. In particular, their second analysis does not contain any bands with deformation vibration in the excited state. In addition, doubt is cast upon their assignment of the origin since there is no band at the position corresponding to the transition $(000)' \leftarrow (001)''$, although bands corresponding to higher vibrational levels of the normal state are assigned. Further comments on their analysis have been made by Price and Simpson.[7]

More recently, with the object of investigating the rotational band structure, the spectrum of sulphur dioxide has been photographed under low, medium and high dispersion in the region λ3900–2600 at various pressures from 0.3 mm to two atmospheres and at 800°, 300° and 200°K. As a result of this survey Metropolis and Beutler[8] established definitely that the electronic transition connected with the weak absorption around λ3800 is distinct from that associated with the stronger contiguous absorption toward shorter wave-lengths. Furthermore, even at pressures of a few millimeters and a dry ice temperature,

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

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

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

[4] J. H. Clements, Phys. Rev. **47**, 224 (1935).

[5] R. K. Asundi and R. Samuel, Proc. Ind. Acad. Sci. **A2**, 30 (1935).

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

[7] W. C. Price and D. M. Simpson, Proc. Roy. Soc. **A165**, 272 (1938).

[8] N. Metropolis and H. Beutler, Phys. Rev. **57**, 1078 (1940).

considerable structure was evident on the long wave-length side of the origin assigned by Clements (which is itself further toward the red than the origin assumed by Samuel and Asundi). This latter fact suggested that the origin must lie at still longer wave-lengths. Finally, the large number of bands excited indicated that the dimensions of the molecule have changed considerably in the electronic transition, so from considerations based on the Franck-Condon principle, one would expect the vibrationless transition to be quite weak.

In view of the foregoing, it was thought advisable to reconsider the vibrational structure of the system around λ3200; the results obtained form the basis of the present work.

EXPERIMENTAL

Sulphur dioxide obtained commercially was distilled twice before being admitted to a reservoir. The Pyrex absorption tube was 4.5 cm in diameter and 1 m in length with flanges at each end. Cylindrical quartz cells of the same diameter as the absorption tube and of 2-cm length with two quartz windows as bases were sealed onto the flanges with Picein. When these cells were evacuated, no water vapor condensed on the windows at low temperatures. From one end of the absorption tube, a side arm was connected to a mercury diffusion pump. At the other, the following were connected in series: stopcock *A*, a small cell whose volume was very nearly 15.9 cc (1/100 the volume of the absorption tube), stopcock *B*, a vertical U-tube, and finally a reservoir.

The U-tube was surrounded by a dry ice-acetone bath. At the equilibrium temperature of CO_2-acetone, the pressure of SO_2 is 8 mm. To obtain pressures less than 8 mm, the small cell was filled with SO_2 at 8 mm pressure, stopcock *A* being kept closed. Then stopcock *B* was closed and *A* opened, allowing the gas to expand into the absorption tube. Thus one could obtain any desired pressure between 0.008 mm and 8.0 mm simply by repeating the operation the required number of times. For higher pressures, crushed dry ice was slowly added to acetone in a thermos flask and sufficiently agitated to obtain a uniform temperature. The absorption tube was then filled at the temperature corresponding to the desired pressure. A pentane thermometer was used (sufficiently accurate here). Finally, a

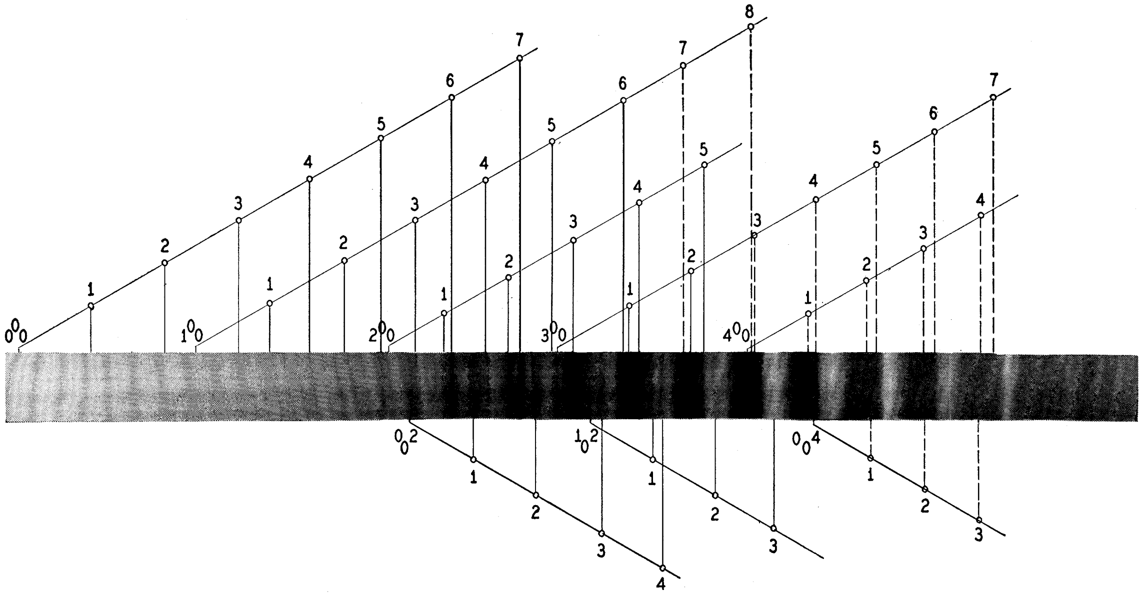

FIG. 1. Spectrogram of SO_2 at 5 mm pressure and 200°K in the region λ3400–2900, taken on the Hilger E1 spectrograph. The vibrational analysis is indicated at the sides of the spectrum; the quantum numbers v'_1, v'_2, v'_3, correspond to the symmetrical valence, the deformation, and the antisymmetrical vibrations respectively. The running numbers are for v'_2. The positions of bands near the system origin have been taken from spectrograms of SO_2 made at higher pressures. The dashed lines correspond to bands calculated by Eq. (1), which is based on bands marked by solid lines.

thermally insulated metal trough, which could be packed with dry ice, surrounded the absorption tube.

For studying the gross features of the electronic system, photographs were taken with a Hilger E3 spectrograph having a dispersion of 15.8A/mm at λ3200 and a Hilger E1 having a dispersion of 5.2A/mm in the same region. The light source used for these photographs was a conventional hydrogen discharge tube carrying 0.8 ampere at 5000 volts. In addition, it was desirable to have photographs taken on the 30-foot grating spectrograph to guide and confirm the vibrational analysis (cf. later discussion and preceding paper[9]). For this purpose a high power tungsten light source[10] was used. For the low dispersion photographs, the exposure time was about three minutes; for medium dispersion, exposures ranged from twenty minutes to an hour. In the region of λ3100 the high dispersion photographs required twenty hours with a slit width of twelve microns. In some cases where it was desired to observe the shape of the band envelopes, the maximum resolving power of 300,000 in the second order of the grating spectrograph was not necessary, and a wide slit of forty microns was used. The high dispersion photographs then required only three hours. Process and Eastman 33 plates were used. An iron arc provided the comparison spectrum.

Description and Analysis of Spectrum

A series of exposures taken under low dispersion at various increasing pressures of SO_2 exhibits a maximum absorption intensity around λ2900 with gradual fading out on both sides. (A photograph of a similar set of SO_2 exposures has been published by Watson and Parker.[2]) As the pressure is increased, the region of marked absorption increases toward both longer and shorter wave-lengths; at atmospheric pressure of SO_2, the long wave-length limit is nearly λ3400. The weaker electronic band system at longer wave-lengths appears at about 50 mm and is well developed at 760 mm. The latter system is more or less clearly separated from the strong absorption region under investigation.

From a study of the vibrational intensity distribution, one may conclude that both apex angle and bond distance have changed considerably in the transition. Consequently, from considerations based on the Franck-Condon principle, the vibrationless transition should be weak. Thus the system origin must lie at longer wave-lengths than the relatively strong bands identified by previous investigators as the vibrationless transition, that is, greater than λ3125. That it does is indeed confirmed by a comparison of spectrograms taken on the Hilger E1 spectrograph at pressures of 0.8 mm, 1.6 mm and 5.0 mm both at room temperature and at dry ice-acetone equilibrium temperature. They show conclusively that the bands lying at wave-lengths longer than λ3125 are definitely *not* from excited vibrational levels but from the vibrationless level in the normal state. The Boltzmann factor for one quantum of the deformation vibration is about 3.5 times smaller at 200° than at 300°K, for two quanta the ratio is 12.25; for one quantum of the ν_1 frequency the ratio is about 15.5. No such changes in intensity were observed for the bands mentioned when the temperature was lowered from 300° to 200°K.

At first it was suspected that the band corresponding to the vibrationless transition, although weak, would be among the bands that appear on the spectrogram taken with 5.0 mm pressure of SO_2 at 200°K. The band of longest wave-length under these conditions is at 30685 cm^{-1}. From this band a progression of quite evenly spaced bands proceeds toward higher frequencies at intervals of approximately 300 cm^{-1}, a spacing which is to be identified with the deformation, or bending, frequency. In addition to the latter progression, another progression, starting approximately in the middle of the first interval of the first progression, proceeds toward shorter wave-lengths with the same intervals. The obvious conclusion is that these two progressions differ by one quantum of the symmetrical valence, or breathing, frequency, and that the origin lies at still longer wave-lengths.

The relative positions of the two progressions indicate that the symmetrical valence frequency ν'_1 is some odd multiple of one-half the deformation frequency ν'_2. It is easily seen that a value near 450 cm^{-1} for ν'_1 is incompatible with the

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[9] N. Metropolis, Phys. Rev. **60**, 283 (1941).

[10] H. Beutler and N. Metropolis, J. Opt. Soc. Am. **30**, 115 (1940).

TABLE I. *Absorption bands of sulphur dioxide. Observed bands and their associated vibrational quantum numbers. The bands without letters or * arising from the vibrationless level of the normal state have been used to determine the coefficients in Eq. (1). The intensity values are those of Clements. In the last column, the mean effective heights of the lower state vibrational levels above the vibrationless level are given as determined by Clements using a temperature variation method. The differences between observed and calculated bands are also given. The calculated values are from Eqs. (1) and (2). All data are for maxima of observed bands. The frequencies of bands labeled with letters or marked with * are taken from Clements, all others are from new measurements. Brackets on left of quantum numbers indicate overlapping bands. Brackets on right indicate that the intensity is to be divided between them. Intensity values in Parentheses are estimated by the author.*

ν	$v'_1v'_2v'_3$	$v''_1v''_2v''_3$	I†	TEMP. VARIATION (CM^{-1})	OBS. ν − CALC. ν
29439	0 1 0	0 1 0	0.3	200	24
29622	0 0 0	0 0 0	0.3		0
29648	1 1 0	0 2 0	0.5		15
29742	0 2 0	0 1 0	0.8		18
29940	0 1 0	0 0 0	1.4	0	0
29994	2 0 0	1 0 0	1.2	1000	−12
30048	0 3 0 0 7 0	0 1 0 1 1 0	1.2	1000	18 −16
30175	1 1 0	0 1 0	(1.2)		16
30249	0 2 0	0 0 0	3	150	0
30280	2 1 0	1 0 0			20
30386	1 0 0 0 6 0	0 0 0 0 2 0	6	300	0 − 7
30435	0 0 1	0 0 0	(1.5)		− 3
30465	1 2 0	0 1 0	(3.0)		15
30551	0 3 0	0 0 0	10	70	− 4
30685	1 1 0	0 0 0	15	50	1
30721	0 1 1	0 0.0	20	0	− 6
30760	1 3 0	0 1 0	(10)		22
30848	0 4 0	0 0 0	25	60	− 8
30980	1 2 0	0 0 0	40	40	4
31037	1 4 0	0 1 0	40	40	17
31125	2 0 0	0 0 0	40	0	−10
31140	0 5 0	0 0 0			−12
31258	0 0 2	0 0 0	(30)		10
31275	1 3 0	0 0 0	(30)		12
31405	2 1 0	0 0 0	60	500	− 8
31430	0 6 0 2 3 0	0 0 0 0 1 0			−13 − 3
31520	0 1 2	0 0 0	65		4
31567	1 4 0		60		22
31675	2 2 0		120		−10
31717	0 7 0		100		−21
31778	0 2 2		80		0
31840	1 5 0		90		16
31855	3 0 0				−14
31940	2 3 0			0	−13
31991	1 0 2		(20)	0	3
32033	0 3 2		(25)	0	− 3
32119	1 6 0		(30)	0	24
32140	3 1 0		(40)	0	9
32198	2 4 0	0 0 0		0	−17
32235	1 1 2		(25)	0	0
32276	0 4 2		(15)	0	−12
32377*C*	1 7 0 3 2 0		600	0	15 − 6
32438	2 5 0		(120)	0	−34
32479	1 2 2		(15)	0	1
32607*D*	1 8 0 3 3 0 4 0 0		600	0	−18 −21 7
32713	1 3 2		(5)	0	− 3
32850*E*	3 4 0 4 1 0 0 0 4		1200	0	−23 12 −18
33080*F*	3 5 0 4 2 0 0 1 4		1700	0	−30 10 − 6
33313*G*	3 6 0 4 3 0 5 0 0 0 2 4		2000	0	−30 15 − 3 15
33547*H*	3 7 0 4 4 0 5 1 0 0 3 4		1900	0	−23 27 13 15
33760*J*	3 8 0 4 5 0 5 2 0		2000	0	−33 22 14
33960*K*	4 6 0 5 3 0		1700	0	10 6
34030*L*	3 9 0 6 0 0		1600	0	20 7
34241*	6 1 0[1]		700	0	20
34180*M*	4 7 0[1] 5 4 0[1]		1600	0	22 24
34396*N*	6 2 0[1]		1600	0	7
34620*O*	6 3 0[1]		1700	0	19
34724*	7 0 0[1]		200	0	3
34785*	6 4 0[1]		1000	0	2
34970*	6 5 0[1]		500	0	9

† Intensity values from Clements (presumably at room temperature).

[1] Possibilities for superposed bands have not been exhausted.

experimental findings. For instance, it is difficult to explain the absence of many bands in case that $\nu'_1 = 450$ cm^{-1} is assumed. In addition, other considerations make this value unlikely. Using 750 cm^{-1} for ν'_1, however, one can identify not only a v'_1 progression but also combination overtones in harmony with the vibrational intensity distribution. Finally, the extrapolated pure v'_1 and pure v'_2 progressions have a common point at 29622 cm^{-1}, which must then be the origin of the band system. The photographs taken at higher pressures of SO_2 confirmed the positions of the origin and of the bands that were too weak on the low pressure photographs.

A band at 31258 cm^{-1} is moderately strong and comparable in intensity to its immediate neighbors. This band cannot be fitted into the scheme of the symmetrical vibrations, and temperature variation data of Clements[4] indicate that it is not from excited levels in the normal state. Assuming that this band corresponds to two quanta of the antisymmetrical frequency ν'_3, one can also explain eight additional bands as combinations of the symmetrical vibrations with two quanta of the antisymmetrical. In addition, a very weak band is found at 30432 cm^{-1}, corresponding to one quantum of the ν'_3 frequency. Although this transition is forbidden by electronic selection rules,[11] it may, nevertheless, be permitted by vibronic selection rules.[12] In a later section, we shall discuss the possibilities for the electronic character of the upper state.

Figure 1 is a reproduction of a spectrogram taken at 200°K and at 5 mm pressure of SO_2, marked with a schematic representation of the vibrational analysis. Bands from excited vibrational levels of the normal state are not labeled in this photograph.

Table I contains a list of the bands according to increasing wave number, with their vibrational quantum number assignments. The wave numbers of the bands labeled *A*, *B*, *C*, ⋯ and of those marked with * are taken from the work of Clements, together with their absorption intensities. However, from only the present measurements, it is found that the vibrational energy levels of the excited state can be represented by the formula

$$\nu = 29622 + 770v'_1 + 320v'_2 + 813v'_3 - 6v'^2_1 \\ - 2.5v'^2_2 - 20v'_1v'_2 - 25v'_2v'_3 - 15v'_1v'_3, \quad (1)$$

where v'_1, v'_2, v'_3 are the symmetrical valence, deformation, and antisymmetrical vibrational quantum numbers respectively. The three fundamental frequencies for the normal state as determined from Raman and infra-red data[13] are

$$\nu''_1 = 1152\ \mathrm{cm}^{-1}, \quad \nu''_2 = 525, \quad \nu''_3 = 1361. \quad (2)$$

In order to account for the prominent series called *A*, *B*, *C*, ⋯ by Clements, Eq. (1) plus the term $+0.15v'^3_1$ have been used to calculate higher members of several progressions, and the results are indicated in Fig. 2 by dashed lines. Thus it is possible to explain the strong progression of Clements, not as a simple v'_2 progression as he did, but by superpositions of various higher combination bands. By application of the Franck-Condon principle, one expects that the pure v'_1 and v'_2 progressions, although of considerable length, do not contain the most intense bands. The latter are found among the combination overtones. Thus the individual bands have already considerable intensity and their superposition effects even higher absorption intensities.

Table I also contains a comparison of the observed and calculated positions of the bands. In the region where the overlapping of intense bands creates a fortuitous appearance of a simple progression, no attempt has been made to identify the various superposed bands individually; instead, the values of the observed maxima are taken from Clements. Better agreement between observed and calculated values cannot be expected for the following reasons: (1) The position of the maximum intensity is used since the location of the band origin is not known; (2) no account is made of resonance

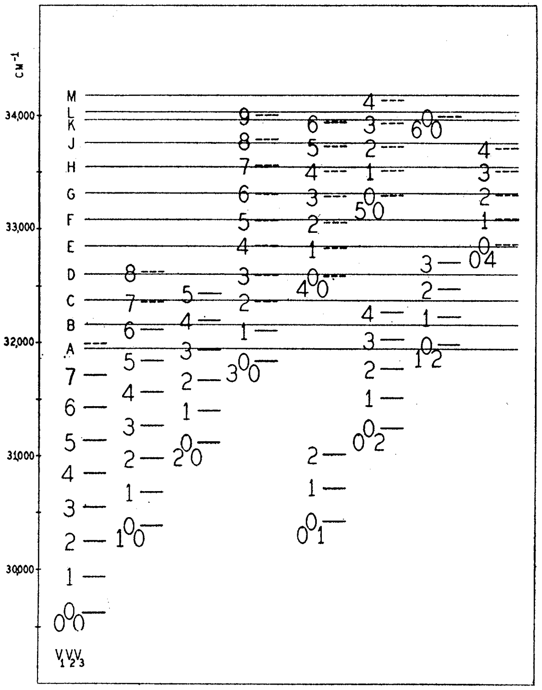

FIG. 2. Vibrational term scheme of the upper electronic state. The bands represented by short solid lines have been used to evaluate the coefficients in Eq. (1). The dashed lines correspond to bands calculated by this equation. Thus the *A*, *B*, *C*, ⋯ absorption regions can be interpreted as superpositions of several bands rather than as a pure v'_2 progression.

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[11] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1938).

[12] Cf. R. S. Mulliken, Phys. Rev. **59**, 873 (1941).

[13] Cf. H. Sponer, *Molekülstruktur* (Julius Springer, Berlin, 1934).

interactions between superposed vibrational levels; (3) overlapping bands arising from low lying excited vibrational levels of the ground state may distort the intensity distribution of a given band appreciably.

Included in Table I are eleven bands which arise from excited levels of the normal state and whose positions are in agreement with what may be calculated from Eq. (1) combined with Eqs. (2).

It was hoped that the photographs taken under high dispersion would exhibit some characteristic feature in the rotational structure, as does the system at λ3880, so that analogous positions in each band could be measured and used instead of the intensity maxima under low dispersion. Unfortunately this was not the case.

DISCUSSION OF RESULTS

When the values of the three upper state fundamental frequencies, $\nu'_1 = 794$ cm^{-1}, $\nu'_2 = 345$ cm^{-1}, $\nu'_3 = 833$ cm^{-1}, are substituted in theoretical formulas based on a valence force model,[14] one obtains two solutions, 100.3° and 79.7°, as possible values for the apex angle. Since there are only seven members of appreciable intensity in the pure v'_2 progression, one is strongly inclined to favor the value of 100.3°.[15] Jonescu[16] from a study of rotational structures in the region λ3000, using the first and second orders of a twenty-one foot grating spectrograph (resolving power not given), reports in a brief communication an apex angle of 96° in the excited and 120° in the normal state. He calculated and plotted band structures assuming various values for α, but keeping the assumed bond distance always fixed at $r = 1.36$A for both electronic states, and compared the results with observed structures. Because, however, of the considerable superposition of bands shown by the present work to exist in the region Jonescu studied, it is very doubtful that any single band can be present there under favorable conditions for investigating the rotational structure; furthermore, calculation shows that the most intense lines for room temperature must be around $J = 20$. Consequently Jonescu's results do not appear to be conclusive, even though there is good agreement of his α' with the value calculated from the fundamental frequencies obtained here.

That the angle has decreased in the upper state is, however, confirmed by the present high dispersion photographs, where the irregular band structures indicate quite definitely that the molecule becomes a more asymmetrical top (see below). The type of structure which would have been expected if the angle had remained unchanged or increased slightly in the transition can be judged from a study of the high dispersion photographs of the λ3880 system of SO_2 and of the figures of the preceding paper.

Clements developed a temperature variation method for determining the heights of initial vibration levels above the vibrationless level. The determination is based on photometric measurements of absorption at two temperatures not too widely separated. The method was first applied to SO_2, and it is interesting to see whether his results are in harmony with the present analysis. Since the various contiguous regions of the spectrum, in which he applied the method, did not overlap, it was possible only for him to compare bands in each region with reference to a fiducial band in that region. However, the present analysis shows that the fiducial bands for all the regions are from the vibrationless level of the normal state. Thus it is possible to compare various regions directly. Referring to the last column of Table I, one sees that the present assignments are in harmony with Clements' data, except, perhaps, for the value of 200 cm^{-1} for $(010)' \leftarrow (010)''$, which lies on the long wave-length side of the vibrationless transition. Very likely, however, an absorption band (arising from the vibrationless level) of the adjacent electronic system overlaps $(010)' \leftarrow (010)''$, giving effectively a value of 200 cm^{-1}.

The considerable overlapping in the absorption regions $A, B, C, \cdots$ may explain why Kusch and Loomis[17] obtained such widely varying magnetic rotation spectra for these "bands."

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

[15] Cf. J. B. Coon, Phys. Rev. **58**, 926(L) (1940). He reported only two bands in a v'_2 progression in ClO_2 corresponding to a change in apex angle from 122° to 114°.

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

[17] P. Kusch and F. W. Loomis, Phys. Rev. **55**, 850 (1939).

The electronic character of the excited state is indicated as singlet by the strong absorption intensity. The presence of two bands in which definitely one quantum of the antisymmetrical vibration is excited, taken in connection with a consideration of the vibronic selection rules, show that the excited state must be either $^1A_1$ or $^1B_2$ (cf. reference 12, Table XI). Were it possible to determine whether the bands under discussion are of the perpendicular or parallel type, one could determine uniquely the nature of the upper electronic state ($^1B_2$ if these bands are of the parallel type, $^1A_1$ if they are perpendicular).

In conclusion, a few remarks may be made concerning the prospects of a rotational analysis of this system. As a result of a decrease in the apex angle ($2\alpha' = 100°$) in the transition, the regularity of symmetric top levels must be entirely lost (cf. Fig. 4 of reference 12), thus rendering the analysis more difficult. In addition, there should be greater overlapping of sub-band structure. Another point is the scarcity of bands free from overlapping; those bands which are intense enough at low pressures, where low temperatures could then be used to reduce the complexity, are considerably overlapped, as we have seen. Those near the system origin require higher pressures to obtain sufficient absorption. The increased pressure precludes work at low temperatures, tends to broaden the rotational lines and makes probable the presence of overlapping, low lying excited vibrational levels of the normal state.

The author is indebted to Professor Robert S. Mulliken and Dr. Hans G. Beutler for helpful suggestions.

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Spectra of Argon in the Extreme Ultraviolet

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A simple method for the excitation of spectra of higher stages of ionization of rare gases is described. Applied to argon, the method has yielded spectra of all stages of ionization from A III to A IX. Classified lines in the extreme ultraviolet and term tables for the ions V to IX are given. Some minor additions and corrections to previous analyses of Cl V and Cl VI are pointed out.

GENERAL AND EXPERIMENTAL

THE extreme ultraviolet spectra of argon have been studied by a number of investigators, the latest work being that of Boyce.[1] References to earlier work may be found in his paper. As a result of these investigations, the spectra of the first four stages of ionization are quite well known. Two multiplets in A V due to transitions from the first excited configuration to the ground state configuration were found by Boyce, but nothing else was known in V or in higher stages. The present investigation was undertaken in the hope of extending the analysis to higher stages of ionization. A preliminary report has already been published.[2]

The method of excitation used is simple and effective. It consists of introducing the gas directly into the space between the two electrodes of an ordinary vacuum spark such as is usually used for the excitation of the spectra of other highly ionized elements. To accomplish this a one-eighth-inch hole is drilled axially into the lower electrode. The gas is fed into the bottom of this hole through a small bronze capillary, which passes through the bottom of the lower electrode holder and is connected to a reservoir in which

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[1] J. C. Boyce, Phys. Rev. **48**, 396 (1935).

[2] W. L. Parker and L. W. Phillips, Phys. Rev. **58**, 93 (1940).

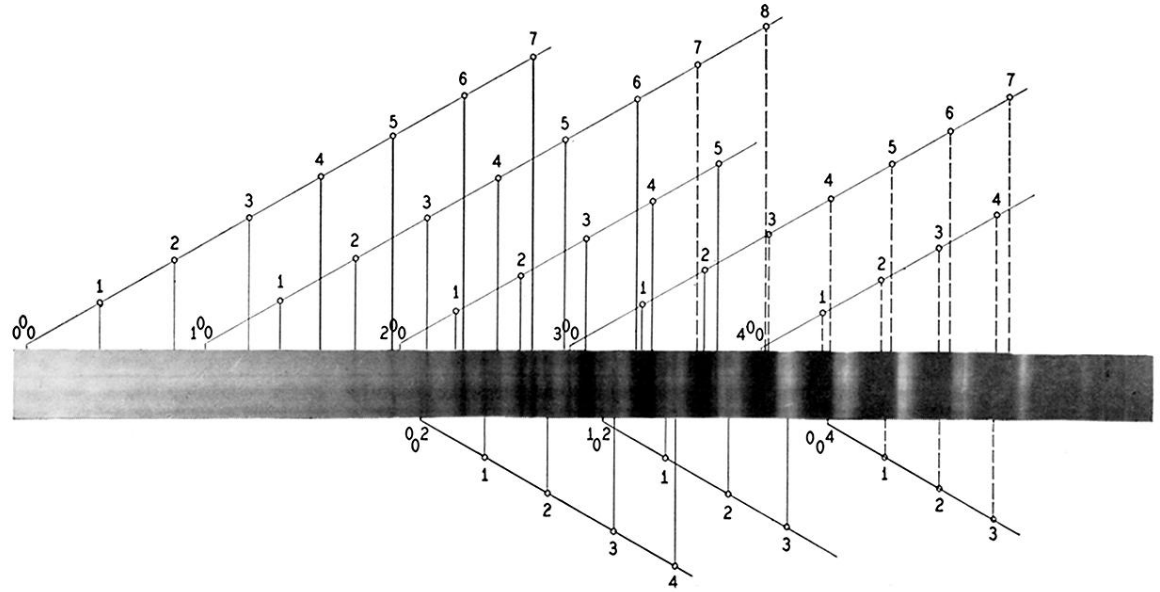

FIG. 1. Spectrogram of SO$_2$ at 5 mm pressure and 200°K in the region λ3400–2900, taken on the Hilger E1 spectrograph. The vibrational analysis is indicated at the sides of the spectrum; the quantum numbers v'_1, v'_2, v'_3, correspond to the symmetrical valence, the deformation, and the antisymmetrical vibrations respectively. The running numbers are for v'_2. The positions of bands near the system origin have been taken from spectrograms of SO$_2$ made at higher pressures. The dashed lines correspond to bands calculated by Eq. (1), which is based on bands marked by solid lines.