THE ROTATIONAL ANALYSIS OF THE S_2 BANDS

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Abstract

The emission spectrum of S_2 has been obtained by means of a Geissler tube, the plates being taken in the third order of a 21 foot concave grating giving a dispersion of 0.878A per mm. The following bands have been studied; 9–1(λ2857.36), 7–0(λ2860.13), 8–1(λ2887.84), 9–2(λ2917.38) and 7–1(λ2920.28). Each band consists of three R and three P branches. For small values of K each band appears to have a weak and a strong R branch and a weak and a strong P branch. The lines of the strong branches separate into two components for $K \geqq 25$. This structure is similar to that of the Schumann-Runge bands of O_2. It is concluded that the S_2 bands investigated are due to a $^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$ transition (like O_2). The values of B_e'' and B_e' (by extrapolation) are 0.409 and 0.319 cm^{-1}, respectively, the nuclear separation of the lower state being $r_e'' = 1.603 \times 10^{-8}$ cm and of the upper state $r_e' = 1.814 \times 10^{-8}$ cm. It is shown that the rotational levels with *odd* K values are missing in the *upper state* and those with *even* K values in the *lower state*. The fact that alternate levels are missing shows that the internal angular momentum of the S^{32} nucleus is zero.

Introduction

THE band spectrum due to the S_2 molecule extends from about λ6000 to λ2300A. The spectrum consists of a large number of overlapping bands which degrade toward the red. These bands have been studied by various investigators. Henri[1] divides the spectrum into four regions according to the frequency equations which fit most accurately the heads obtained in absorption. Rosen[2] has shown, however, that all these bands belong to the same band system, and from the vibrational analysis obtained the following equation for the heads:

$$\nu = \nu_e + 427.1(v' + \tfrac{1}{2}) - 2.7(v' + \tfrac{1}{2})^2 - 727.4(v'' + \tfrac{1}{2}) + 2.91(v'' + \tfrac{1}{2})^2 \quad (1)$$

Henri[1] found the bands to become diffuse at λ2794.2, a phenomenon which he termed "predissociation."

Henri and Teves[3] using plates taken in absorption with relatively small dispersion, attempted a rotational analysis of the S_2 spectrum. They state that each band consists of P, Q, and R branches, giving the values of the nuclear separations for the upper and lower states as $r' = 0.70$A and $r'' = 0.73$A. Teves[4] continued this work in fluorescence obtaining results similar to those of Henri and Teves. Recently Swings[5] and Rompe[6] also working with the

[1] V. Henri, Structure des Molecules, Paris, p. 93 (1925).
[2] B. Rosen, Zeits. f. Physik **43**, 69 (1927).
[3] V. Henri and M. C. Teves, C. R. **179**, 1156 (1924).
[4] M. C. Teves, Dissertation, Zurich (1926).
[5] P. Swings, Zeits. f. Physik **61**, 681 (1930).
[6] R. Rompe, Zeits. f. Physik **65**, 404 (1930).

fluorescence spectrum of S_2, have tried to bring their results into agreement with those of Henri and Teves, but found it impossible to interpret completely the complex patterns obtained.

It has been shown that the molecules F_2, Cl_2, Br_2, and I_2 have similar electronic states. The same has also been found in the molecules Li_2, Na_2, and K_2.[7] One would therefore expect a corresponding similarity to hold for O_2 and S_2. In particular it seems probable that the S_2 bands mentioned above are analogous to the Schumann-Runge bands of O_2. Recently E. V. Martin and F. A. Jenkins[8] have also found the SO bands lying between λ2500 and λ3500 to correspond to the Schumann-Runge bands. The analysis of Henri and Teves, however, would indicate that S_2 differs fundamentally from O_2. Furthermore, the values of r_e'' and r_e' found for the O_2 Schumann-Runge bands[9,10] are 1.204 and 1.609A, respectively. Irrespective of the similarity of the S_2 and O_2 bands, the values of the nuclear separations for the two states obtained by Henri are too small, since the r_e values for S_2 are surely greater than those for O_2, whereas, according to Henri, the reverse is the case.

The purpose of the present work was to check Rosen's results by studying the spectrum of the S_2 bands photographed with greater dispersion than he used, and to obtain the rotational analysis. The work dealing with the vibrational analysis, perturbations, predissociation, etc., will be discussed in a later paper, and only that concerning the rotational structure will be given here. It will suffice to state that, except for the revision of the vibrational quantum numbers of a number of band heads and the discovery of numerous perturbations, mainly in the upper electronic state, our results agree with those of Rosen, so that his analysis with a few modifications can be made use of in the present paper.[11]

Experimental Procedure

The spectrum of S_2 was excited in a Geissler tube (see Fig. 1) of Pyrex, having large cylindrical aluminum electrodes, so that as much as 0.7 amps. could be passed through the tube. The current was supplied by a 5 KW transformer. The tube was provided with a quartz window W sealed on to one end of a quartz tube, the other end of which was ground flat. This end of the quartz tube was sealed onto the Pyrex tube with sealing wax. Considerable difficulty was experienced in keeping the quartz window from fogging due to sulphur condensing on it. The best results were obtained when the sulphur was introduced into the tube in the form of H_2S [12] which streamed continuously through the tube in the direction away from the window, thus opposing the diffusion of sulphur towards the window. In case the window did get fogged with sulphur, heating it gently with a bunsen burner restored

[7] R. S. Mulliken, Phys. Rev. **36,** 1440 (1930).

[8] E. V. Martin and F. A Jenkins, Phys Rev. **37,** 226 (1931).

[9] W. Ossenbrüggen, Zeits. f. Physik **49,** 167 (1928).

[10] W. Lochte-Holtgreven and G. H. Dieke, Ann. d. Physik (5) **3,** 937 (1929).

[11] P. Huber, Amer. Phys. Soc. Meeting, Paper No. Q5, Cleveland. Dec. 30, 1930, has apparently also found that Rosen's vibrational analysis is fundamentally correct.

[12] H. H. Van Iddekinge (Nature **125**, 858 (1930)) has independently used the same method.

its transparency. The H_2S was dried over P_2O_5 before introduction into the tube. In the discharge tube the H_2S dissociated, giving sulphur and hydrogen.[13] The other end of the tube was connected to a liquid air trap in which the sulphur and H_2S were frozen out. This trap in turn was connected to a Megavac oil pump which was kept running while the discharge was going on. The pressure of the sulphur in the discharge tube could be regulated by controlling the flow of H_2S by means of a stopcock sealed on to a capillary tube.

Another method used for introducing the sulphur into the above discharge tube was by distilling the sulphur in vacuo into the side tube T (see Fig. 1). By heating T while the discharge was running pure sulphur could be introduced directly into the discharge tube. In this case a mercury diffusion pump was used to evacuate the discharge tube beforehand. More sulphur condensed on the window when this method was used and therefore the former method was preferred for long exposures. The spectrum obtained by

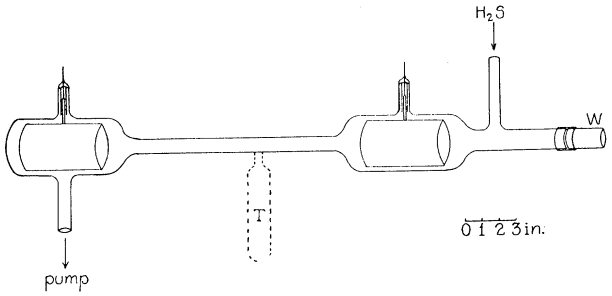

Fig. 1. Discharge tube used for obtaining the S_2 emission spectrum in the region λ2850 −λ2950 with great intensity. W is a quartz window sealed into a quartz tube which is in turn sealed on to the discharge tube with sealing wax. When sulphur is used instead of H_2S to obtain the spectrum the tube T with the dotted outline contains pure sulphur.

this method agreed with that obtained by introducing H_2S, as was determined by comparing plates taken in the second order of the 21 foot grating in both cases.

The photographs of the bands in the region λ2850–λ2950 used for the analysis were taken in the third order of the 21 foot Rowland grating giving a dispersion of 0.878A per mm. A red purple filter of the Corning Glass Company was used to cut out the second order between λ4250 and λ4450A which would otherwise overlap the spectrum obtained. Eastman 33 plates were used. The time of exposure was about 30 hours.

The plates were measured on a comparator with an accuracy of 0.003 mm. The iron arc was used as comparison spectrum, the wave-lengths of which were taken from Kayser's "Hauptlinien" (1926). The iron standards agreed to within 0.003A, so that the wave-lengths of the sulphur band lines

[13] In the region λ2850 −λ2950, which we studied for this work, the sulphur spectrum was very intense as compared with the weak continuous spectrum obtained from the hydrogen molecule.

may be assumed to be correct to 0.01A. The wave-lengths (in air) were converted to wave-numbers (in vacuo) by means of Kayser's "Schwingungszahlen."

Data and Rotational Analysis

The bands due to S_2 are very numerous so that there is practically no region of the emission spectrum in which overlapping does not occur. In the region between λ2828 and λ2950 the overlapping is the least. Therefore the bands: 9–1, with its head at λ2857.36; 7–0, λ2860.13; 8–1, λ2887.84; 9–2, λ2917.38 and 7–1, λ2920.28, have been chosen for the rotational analysis. Even with the large resolution used a large number of lines could not be separated, a few unresolved groups having a width as large as 1 cm^{-1}. The lines of the 9–1 and 9–2 bands could not be followed very far due to the overlapping of the 7–0 and 7–1 bands, the latter being considerably more intense than the former. Other weaker bands are partially superposed on the 8–1, the 7–1 and probably on the 7–0 band, making the assignment of the lines into series extremely difficult.

It was noticed that in the clear regions of the 9–1 and 9–2 bands the strong lines in each band could be assigned into two distinct series. For every strong line in the above bands there is a line of about half the intensity on the short wave-length side of the former, the interval between the strong and the weak lines remaining approximately constant. The same type of series, i.e. two strong and two weak series, has been found in each of the remaining bands. In the two bands, 7–0 and 7–1, in which the series could be followed to a considerable distance from the head, it was seen that each line of the strong series splits into two lines, the components of this doublet having equal intensity. The distance between each line of the weak series and the center of the corresponding doublet in the strong series, after its lines had split, is the same as before splitting occurred. In this region the three lines, i.e. the lines of the weak series and the two corresponding lines into which each line of the strong series splits, are approximately of the same intensity. It is evident, therefore, that each band consists of six series: A , A_y, A_z, B_x, B_y and B_z. In the 9–1 and 9–2 bands, where the overlapping by other bands is least, all lines but two have been assigned to the various branches.

The two sets of combinations which are given in Tables IV and V were obtained by performing the subtraction $A(\alpha)-B(\beta)$ and $A(\alpha)-B(\beta+1)$, where α and β are arbitrary numbers assigned to the series A and B respectively. Since the S_2 bands are those of a homopolar molecule $(S^{32})_2$, we may expect alternate band lines to be either missing or weak.[14] But if the latter were the case we would have noticed it. If, however, all lines are present in the series, the above combinations would correspond to $R(K)-Q(K)\approx\Delta_1F'(K)$ and $R(K)-Q(K+1)\approx\Delta_1F''(K)$, [or $Q(K)-P(K)\approx\Delta_1F'(K)$ and $Q(K)-$

[14] F. W. Aston (Proc. Roy. Soc. **A115,** 487 (1927)) has estimated that about 97 percent of the atomic weight of sulphur is due to the S^{32} isotope. Consequently these S_2 bands must be due to $(S^{32})_2$. The bands due to $S^{32}S^{34}$ and $S^{32}S^{33}$ have not been observed. These bands will be very much weaker and, furthermore their calculated positions lie within the bands investigated thus making their observation more difficult.

$P(K+1) \approx \Delta_1 F''(K)$]. The A_x, A_y, and A_z series would then be three R (or three Q) branches and the B_x, B_y and B_z series would be three Q (or three P)

TABLE I. *Wave-numbers of the lines in the 9–1 and 9–2 bands and the intervals between corresponding strong and weak lines*

	9-1 band				9–2 band			
K	R	P	$\delta\nu_R$	$\delta\nu_P$	R	P	$\delta\nu_R$	$\delta\nu_P$
3	—	34983.2* 82.3	—	−0.9	—	34263.4* 62.4	—	−1.0
5	34987.1* —	980.8* 79.7	—	−1.1	34267.4* 66.5	261.0* 60.0	−0.9	−1.0
7	986.3* 84.7	977.4* 76.4	−1.6	−1.0	266.5* 65.5	257.7* 56.6	−1.0	−1.1
9	985.2* 84.2	973.4* 72.1	−1.0	−1.3	265.2* 64.3	253.6* 52.6	−0.9	−1.0
11	983.2* 82.3	969.1* 68.0	−0.9	−1.1	263.4* 62.4	249.3* 48.3	−1.0	−1.0
13	980.8* 79.7	964.0*[1] 62.8	−1.1	−1.2	261.2* 60.0	244.7* 43.3	−1.2	−1.4
15	978.1* 76.4	958.2* 57.0	−1.7	−1.2	257.9* 56.7	238.7* 37.2	−1.2	−1.5
17	974.2* 72.7[1]	952.3* 50.7	−1.5	−1.6	254.4* 52.9	232.6* 31.1	−1.5	−1.5
19	970.0* 68.6	945.1* 43.6	−1.4	−1.5	250.4* 49.3	225.2* 24.0	−1.1	−1.2
21	965.3* 63.7[1]	937.4* 35.9	−1.6	−1.5	245.8* 44.7	218.0* 17.1	−1.1	−0.9
23	959.9* 58.2	929.6* 28.0	−1.7	−1.6	240.2* 38.7	210.0* 08.6	−1.5	−1.4
25	954.0* 52.7	921.9 21.4[1] 20.0[1]	−1.3	−1.6	234.5* 33.3	201.4* 00.0	−1.2	−1.4
27	947.2* 45.5[1]	— 911.6 09.9	−1.7	−1.7	228.1* 26.8	193.0 92.5 91.5	−1.3	−1.3
29	—	—	—	—	222.4 21.7 20.4	183.9 83.2 82.1	−1.6	−1.4
31	—	—	—	—	214.7 14.0 12.7	173.6 73.0 72.0	−1.6	−1.3
33	—	—	—	—	—	163.1 62.5 61.2	—	−1.6

* These lines are made up of two components which become resolvable at $K=25$. They are referred to in the text as R_{xy} and P_{xy}, and when they become resolvable R_x, R_y, P_x and P_y. The remaining values are then R_z and P_z. It will be shown later in the text that R_x, R_y and R_z correspond to R_1, R_3 and R_2, respectively, and similarly for the P branches.

[1] Smoothed values, the observed lines being composite.

branches. But if alternate lines are missing, the combinations correspond to $R(K)-P(K)=\Delta_2F'(K)$ and $R(K)-P(K+2)=\Delta_2F''(K+1)$. The equations for Δ_1F and Δ_2F are:

$$\Delta_1F = \text{constant} + 2(B + 3D)K + 4DK^3 \quad (2)$$

$$\Delta_2F = \text{constant} + 4(B + 3D)K + 8DK^3 \quad (3)$$

where $B=h/8\pi^2\mu cr^2$ and $D=-4\overline{B}^3/\omega_e^2$, μ being the reduced mass of the molecule. If we assume the first alternative, i.e. no lines missing, we obtain from our data $B''=0.818$ cm^{-1}, while the second gives $B''=0.409$ cm.$^{-1}$ From the empirical formula[15] $B=(27.7/\mu)\ (3000/\omega'')^{-2/3}$ which holds within a few percent for all known molecules composed of atoms of equal or nearly equal mass, we obtain $B''=0.404$ cm.$^{-1}$ Furthermore, if we assume that all lines are present, the value of D calculated from the theoretical relation $D_e=-4B_e^3/\omega_e^2$ is sixteen times as large as the value actually obtained from our data, whereas if we assume alternate lines missing, the value of D obtained from our data agrees within experimental error with the above theoretical value. These comparisons show that we must adopt Δ_2F and alternate missing lines. The series A and B therefore correspond to three R and three P branches.

In Tables I, II, and III, listed under their respective headings, R or P, are given the lines of the five bands investigated. The lines indicated by asterisks are the strong lines made up of two components which become resolvable at about $K=25$. The values with superscript (1) are assumed values, the observed lines being composite. $\delta\nu_R$ and $\delta\nu_P$ are the intervals between the weak and the strong lines in the R and P branches, except that where the strong lines are separated into two components, $\delta\nu$ is the interval between the weak line and the center of gravity of the doublet. It is seen that these intervals are the same within experimental error for all the bands investigated.

The values of $\Delta_2F''(K)=R(K-1)-P(K+1)$, which should agree for the $7-1$, $8-1$ and $9-1$ bands are given in Table IV B. In Tables IV A and IV C the corresponding Δ_2F'''s of 7–0 and 9–2 are tabulated. The values of $\Delta_2F'(K)$ which should agree for the 7–1 and 7–0, and for the 9–1 and 9–2 bands are given in Table VA and VC. The corresponding $\Delta_2F'(K)$'s for the 8–1 bands are given in Table VB. It will be seen that all the expected agreements are fulfilled within experimental error.

The absence of strong Q branches indicates that we are dealing with a transition for which $\Delta\Lambda=0$. Furthermore, the great intensity of the entire system makes it evident that the transition is between two states of equal multiplicity, i.e. $\Delta S=0$. From the structure of the band, three R and three P branches, we conclude that the electronic states involved are triplets. The possible transitions are $^3\Sigma\rightarrow{}^3\Sigma$, $^3\Pi\rightarrow{}^3\Pi$ and perhaps $^3\Delta\rightarrow{}^3\Delta$.[16] The fact that

[15] P. M. Morse, Phys. Rev. **34**, 57 (1929).

[16] In a $^3\Pi\rightarrow{}^3\Pi$ or $^3\Delta\rightarrow{}^3\Delta$ transition we would expect three strong R and three strong P branches present, spaced approximately as in a $^3\Sigma\rightarrow{}^3\Sigma$ transition, if we have case (b) for both upper and lower electronic states, or if we had case (a) in which A is approximately the same in both the upper and the lower states (cf. TiO bands: A. Christy, Phys. Rev. **33**, 701 (1929)). For these transitions, however, we would expect all lines to be present and also the so called staggering effect, the magnitude of which would depend on λ type doubling.

TABLE II. *Wave-numbers of the lines in the 7–0 and 7–1 bands and the intervals between corresponding strong and weak lines.*

	7–0 band				7–1 band			
K	R	P	$\delta\nu_R$	$\delta\nu_P$	R	P	$\delta\nu_R$	$\delta\nu_P$
3	—	34949.9* 48.2	—	−1.7	—	34230.0* 29.0	—	−1.0
5	34953.3* —	947.2* 45.5	—	−1.7	34233.3* 31.9	227.6* 26.0	−1.4	−1.6
7	952.7* 51.0[1]	944.2* 42.8	−1.7	−1.4	232.6* 31.1	224.2* 22.8	−1.5	−1.4
9	951.6* 50.2	940.5* 39.2	−1.4	−1.3	231.9* 30.4	220.4* 19.0	−1.5	−1.4
11	949.9* 48.2	935.7* 34.1	−1.7	−1.6	230.0* 29.0	215.8* 14.4	−1.0	−1.4
13	947.2* 45.5	930.6* 29.2	−1.7	−1.4	227.6* 26.0	210.8* 09.2	−1.6	−1.6
15	943.6* 42.0[1]	924.3* 22.7	−1.6	−1.6	223.6* 21.7	204.7* 03.2	−1.9	−1.5
17	939.4* 37.8[1]	917.7* 15.9	−1.6	−1.8	219.5* 18.0	197.8* 95.9	−1.5	−1.9
19	934.1* 32.6	909.9* 08.2	−1.5	−1.7	214.4* 12.7	190.3* 88.5	−1.7	−1.8
21	928.7* 27.1	901.5* 00.5	−1.6	−1.0	208.6* 07.6	182.1* 80.3	−1.0	−1.8
23	921.9* 20.5	892.9* 91.5	−1.4	−1.4	201.4* 00.4	173.0* 71.9	−1.0	−1.1
25	914.4 14.0[1] 12.8	883.0 82.6 81.5	−1.4	−1.3	194.5* 93.4	163.1* 61.8	−1.1	−1.3
27	906.4 05.6 04.3	872.6 71.8 71.0	−1.7	−1.2	186.2 86.0 84.7	153.0 52.4 51.4	−1.4	−1.3
29	34898.1 97.2 96.2	34862.4 61.5 60.2	−1.4	−1.7	34177.8 77.0 75.5	34141.5 40.8 39.4	−1.9	−1.7
31	888.7 87.5 86.8	849.8 48.5 47.6	−1.3	−1.5	167.8 66.9 65.5	128.8 27.8 26.4	−1.8	−1.9
33	877.6 76.7 75.7	836.6 35.2 34.4	−1.4	−1.5	157.0 56.5 55.0	116.2 15.3 14.3	−1.7	−1.4
35	865.9 65.0 64.3	822.5 21.1 20.5	−1.2	−1.3	145.7 44.8 44.0	102.2 101.7 00.4	−1.3	−1.3
37	—	—	—	—	—	088.2 86.8 86.1	—	−1.4

* These lines are made up of two components which become resolvable at $K=25$. They are referred to in the text as R_{xy} and P_{xy}, and when they become resolvable R_x, R_y, P_x and P_y. The remaining values are then R_z and P_z. It will be shown later in the text that R_x, R_y and R_z correspond to R_1, R_3, and R_2, respectively, and similarly for the P branches.

[1] Smoothed values, the observed lines being composite.

alternate lines are missing instead of staggering and that only three R and three P branches are present[17] clearly indicates that the bands are due to a

TABLE III. *Wave-numbers of the lines in the* 8–1 *band and the intervals between corresponding strong and weak lines.*

K	8–1 band R	8–1 band P	$\delta\nu_R$	$\delta\nu_P$
3	—	34614.1*	—	−1.7
		12.4		
5	34617.7*	612.0*	−1.4	−1.1
	16.3	10.9[1]		
7	616.9*	608.9*	−1.3	−1.8
	15.6	07.1		
9	616.3*	604.4*	−1.4	−1.6
	14.9	02.8		
11	614.1*	599.7*	−1.7	−1.1
	12.4	98.6		
13	612.0*	594.8*	−1.4	−1.4
	10.6	93.4		
15	608.9*	589.6*	−1.8	−1.3
	07.1	88.3		
17	604.4*	583.0*	−1.6	−1.5
	02.8	81.5		
19	599.7*	575.4*	−1.1	—
	98.6	—		
21	594.0*	567.4*	−1.6	−1.4
	92.4	66.0		
23	588.3*	558.8*	−1.5	−1.2
	86.8	57.6		
25	581.5*	549.7*	−1.7	−1.2
	79.8	48.5		
27	573.5*	539.0*	−1.4	−1.4
	72.1	37.6		
	565.9	529.6		
29	65.2	28.5	−1.8	−1.8
	63.7	27.2		
	—	516.8		
31	555.1	16.1	−1.6	—
	53.5	—		

* These lines are made up of two components which become resolvable at $K=29$. They are referred to in the text as R_{xy} and P_{xy}, and when they become resolvable R_x, R_y, P_x, and P_y. The remaining values are then R_z and P_z. It will be shown later in the text that R_x, R_y and R_z correspond to R_1, R_3 and R_2, respectively, and similarly for the P branches.

[1] Smoothed values, the observed lines being composite.

$^3\Sigma \rightarrow {}^3\Sigma$ transition, presumably analogous to that of the Schumann-Runge bands of O_2. We also know that the final $^3\Sigma$ state is the normal state, because these bands are observed with great intensity in absorption.[18,1,2]

[17] ^RQ and ^PQ band lines would probably be too weak to detect.

[18] We have found that this system of S_2 appears with great intensity in absorption.

TABLE IV. *The values of Δ_2F'' for the levels in which $v''=0$, 1 and 2.*

K	*A* 0″ level 7–0	7–1	*B* 1″ level 8–1	9–1	*C* 2″ level 9–2
6	9.1*	9.1*	8.8*	9.7*	9.7*
	—	9.1	9.2	—	9.9
8	12.2*	12.2*	12.5*	12.9*	12.9*
	11.8	12.1	12.8	12.6	12.9
10	15.9*	16.1*	16.6*	16.1*	15.9*
	16.1	16.0	16.3	16.2	16.0
12	19.3*	19.2*	19.3*	19.2*	18.7*
	19.0	19.8	19.0	19.5	19.1
14	22.9*	22.9*	22.4*	22.6*	22.5*
	22.8	22.8	22.3	22.7	22.8
16	25.9*	25.8*	25.9*	25.8*	25.3*
	26.1	25.8	25.6	25.7	25.6
18	29.5*	29.2*	29.0*	29.1*	29.2*
	29.6	29.5	—	29.1	28.9
20	32.6*	32.3*	32.3*	32.6*	32.4*
	32.1	32.4	32.6	32.7	32.2
22	35.8*	35.6*	35.2*	35.7*	35.8*
	35.6	35.7	34.8	35.7	36.1
24	39.3*	38.3*	38.6*	38.5*	38.8*
	39.0	38.6	38.3	38.2	38.7
26	{41.8	—		—	
	{42.2	42.1	42.5*	42.4	42.0*
	41.8	42.0	42.2	42.8	41.8
28	{44.0	{44.7	—		—
	{44.1	{45.2	45.0		44.9
	44.1	45.3	44.9		44.7
30	{48.3	{49.0	{49.1		{48.8
	{48.7	{49.2	{49.1	—	{48.7
	48.6	49.1	—		48.4
32	{52.1	{51.6			{51.6
	{52.3	{51.6	—	—	{51.5
	52.4	51.2			51.5
34	{55.1	{54.8			
	{55.6	{54.8	—	—	—
	55.2	54.6			
36	—	{57.5			
		{58.0	—	—	—
		57.9			

* These values are obtained from the stronger R and P branches before the lines become resolvable, and are referred to in the text as Δ_2F_{xy}. The bracketed values are then Δ_2F_z and Δ_2F_y. The remaining values are Δ_2F_x. As will be shown later in the text Δ_2F_x, Δ_2F_y and Δ_2F_z correspond to Δ_2F_1, Δ_2F_3 and Δ_2F_2, respectively.

The rotational levels of a $^3\Sigma$ state are given by[19]

$$F_i = B_vK(K+1) + f_i(K, J-K) + D_vK^2(K+1)^2 + \quad (4)$$

[19] For a detailed discussion cf. R. S. Mulliken, Rev. Modern Physics **2**, 105 (1931.) The factor G has been omitted in Eq. (4).

TABLE V. *The values of Δ_2F' for the levels in which $v'=7$, 8 and 9.*

	A 7′ level		*B* 8′ level	*C* 9′ level	
K	7–0	7–1	8–1	9–1	9–2
5	6.1*	5.7*	5.7*	6.3*	6.4*
	—	5.9	5.4	—	6.5
7	8.5*	8.4*	8.0*	8.9*	8.8*
	8.2	8.3	8.5	8.3	8.9
9	11.1*	11.5*	11.9*	11.8*	11.6*
	11.0	11.4	12.1	12.1	11.7
11	14.2*	14.2*	14.4*	14.1*	14.1*
	14.1	14.6	13.8	14.3	14.1
13	16.6*	16.8*	17.2*	16.8*	16.5*
	16.3	16.8	17.2	16.9	16.7
15	19.3*	18.9*	19.3*	19.9*	19.2*
	19.3	18.5	18.8	19.4	19.5
17	21.7*	21.7*	21.4*	21.9*	21.8*
	21.9	22.1	21.3	22.0	21.8
19	24.2*	24.1*	24.3*	24.9*	25.2*
	24.4	24.2	—	25.0	25.3
21	27.2*	26.5*	26.6*	27.8*	27.8*
	26.6	27.3	26.4	27.8	27.6
23	29.0*	28.4*	29.5*	30.3*	30.2*
	29.0	28.5	29.2	30.2	30.1
25	{31.4				
	{31.4	31.4*	31.8*	32.6*	33.1*
	31.3	31.6	31.3	32.7	33.3
27	{33.8	{33.2			
	{33.8	{33.6	34.5*	35.6	35.6
	33.3	33.3	34.5	35.6	35.3
29	{35.7	{36.3	{36.3		{38.5
	{35.7	{36.2	{36.7	—	{38.5
	36.0	36.1	36.5		38.3
31	{38.9	{39.0	—		{41.1
	{39.0	{39.1	39.0	—	{41.0
	39.2	39.1	—		40.7
33	{41.0	{40.8			
	{41.5	{41.2	—	—	—
	41.3	40.7			
35	{43.4	{43.5			
	{43.9	{43.1	—	—	—
	43.8	43.6			

* These values are obtained from the stronger R and P branches before the lines become resolvable, and are referred to in the text as Δ_2F_{xy}. The bracketed values are then Δ_2F_x and Δ_2F_y. The remaining values are Δ_2F_z. As will be shown later in the text Δ_2F_x, Δ_2F_y and Δ_2F_z correspond to Δ_2F_1, Δ_2F_3 and Δ_2F_2, respectively.

Where J is the total angular momentum of the molecule, its values being $J=K+S$, $K+S-1$, . . . , $K-S$. S is the resultant electronic spin. For a

triplet state $S=1$, hence $J=K+1$, K and $K-1$. Due to the three values of J, we shall have, in general, three closely spaced energy states for each value of K. These energy states are designated by F_1, F_2 and F_3, where F_1 corresponds to $J=K+1$, F_2 to $J=K$ and F_3 to $J=K-1$.

As has been shown by Kramers,[20] $f_i(K, J-K)$ for ${}^3\Sigma$ states is made up of two parts, one of which is due to the interaction of the resultant electronic spin $\mathbf{S}^*$ with the rotational angular momentum $\boldsymbol{K}^*$, and is equal to

$$(1/2)\gamma[J(J+1) - K(K+1) - S(S+1)] = (1/2)\gamma[(J(J+1) - K(K+1) - 2] \quad (5)$$

while the other part is due to the interaction between the individual spins of the electrons and is designated by $w_i(K, J-K)$. $f_i(K, J-K)$ then becomes

$$f_i(K, J-K) = (1/2)\gamma[J(J+1) - K(K+1) - 2] + w_i(K, J-K) \quad (6)$$

It has been shown [20] that $w_i(K, J-K)$ has the following form for the three values of J:

$$J = K+1, \quad w_1 = -\epsilon(1 - 3/2K + 3) \quad (7)$$

$$J = K-1, \quad w_3 = -\epsilon(1 + 3/2K - 1) \quad (8)$$

$$J = K, \quad w_2 = +2\epsilon. \quad (9)$$

We can neglect terms in ϵ/K for moderate and large values of K, since ϵ is usually small. $f_i(K, J-K)$ then is:

$$J = K+1, \quad f_1 = -\epsilon + \gamma K \quad (10)$$

$$J = K-1, \quad f_3 = -\epsilon - \gamma(K+1) \quad (11)$$

$$J = K, \quad f_2 = 2\epsilon - \gamma \quad (12)$$

The lines of the R and P branches are given by:

$$R_i(K) = \nu^0 + F_i'(K+1) - F_i''(K) \quad (13)$$

$$P_i(K) = \nu^0 + F_i'(K-1) - F_i''(K) \quad (14)$$

Hence, for the three components of the triplet,

$$\Delta_2 F_i'(K) = R_i(K) - P_i(K) = F_i'(K+1) - F_i'(K-1) \text{ is:}[21]$$

$$J = K+1, \quad \Delta_2 F_1'(K) = 2(B_v' + 2D_v' + \gamma') + 4(B_v' + 3D_v')K + 8D_v'K^3 \quad (15)$$

$$J = K-1, \quad \Delta_2 F_3'(K) = 2(B_v' + 2D_v' - \gamma') + 4(B_v' + 3D_v')K + 8D_v'K^3 \quad (16)$$

$$J = K, \quad \Delta_2 F_2'(K) = 2(B_v' + 2D_v') + 4(B_v' + 3D_v')K + 8D_v'K^3 \quad (17)$$

For the lower electronic state,

[20] H. A. Kramers, Zeits. f. Physik **53**, 422 (1929).

[21] We should include in these equations an additional term $+12\, D_v\, K^2$; but D_v is of the order of magnitude of 10^{-7}, so that, for values of K in which this term will become appreciable, the contribution of the cubic term will be much greater than that of the squared term, and hence the latter may be neglected.

$\Delta_2F_i''(K) = R_i(K+1) - P_i(K-1) = F_i''(K+1) - F_i''(K-1)$ has exactly the same form as in the above equations, except that the (′) is replaced by the (″).

In Tables IV and V the Δ_2F values with asterisks, Δ_2F_{xy}, are obtained from the lines of the strong R and P branches. When these lines are resolvable, the bracketed values, Δ_2F_x and Δ_2F_y, for any one K, are obtained from the corresponding components of the doublets. The remaining value Δ_2F_z for every K is obtained from the weak R and P branches. As will be shown later, Δ_2F_z corresponds to Δ_2F_2, cf. Eq. (17). The sets of values Δ_2F_{xy} correspond to the mean of Eqs. (15) and (16), i.e. $\overline{\Delta_2F_{13}(K)} = 2(B_v+2D_v)+4(B_v+3D_v)K+8D_vK^3$ which is the same as Eq. (17). If we assume γ negative (the justification will be discussed below) Δ_2F_1 and Δ_2F_3, cf. Eqs. (15) and (16), correspond to Δ_2F_x and Δ_2F_y, respectively.

The values of the molecular constants obtained from the data are listed in Table VI. The values of B were obtained from the slopes of our graphs corresponding to Eqs. (15), (16) and (17). The value of D_e was obtained from the equation $D_e = -4B_e^3/\omega_e^2$, which agrees within experimental error with the value obtained from Eqs. (15), (16), and (17).

$$B_e = B_0 + \tfrac{1}{2}\alpha_e \quad \text{and} \quad \alpha_e = \frac{B_0 - B_v}{v}$$

TABLE VI. *Values of molecular constants.*

		B (cm^{-1})	D_e (cm^{-1})	α_e B_e and r_e[22]	ϵ and γ[23]
$^3\Sigma_g^-$	$v''=0$	0.408_3	$D_e''=$	$\alpha_e=0.000_7$	$\epsilon'-\epsilon''=0.47$
	$v''=1$	0.407_7	-5.2×10^{-7}	$B_e''=0.409$ cm^{-1}	$\gamma'\approx\gamma''\approx-0.1$
	$v''=2$	0.407_0		$r_e''=1.603\times10^{-8}$cm	$\gamma-\gamma''=$ $\pm0.014\pm0.003$
$^3\Sigma_u^-$	$v'=0$	0.318_5 (extrapolated)			
	$v'=7$	0.308	$D_e'=$	$\alpha_e=0.001_5$	
	$v'=8$	0.306	-7.2×10^{-7}	$B_e'=0.319$ cm^{-1}	
	$v'=9$	$\begin{cases}0.305\\0.341\end{cases}$		$r_e'=1.814\times10^{-8}$cm	

The experimental values of Δ_2F for $v'=9$ obtained from the $9-1$ and $9-2$ bands do not fall upon a straight line as one would expect. In order to represent these points we had to drawn two straight lines, one fitting the points for lower values of K giving $B_9'=0.305$ cm,$^{-1}$ and the other fitting the points for higher values of K giving $B_9'=0.341$ cm.$^{-1}$ It is thought that this effect is due to the perturbation of the rotational levels. This seems plausible, for

[22] In our letter, Phys. Rev. **36,** 1800 (1930), the values of r_e are incorrectly given due to an arithmetical error in obtaining the r_e values from the values of B_e.

[23] The constants ϵ and γ are discussed in the following section. From our data we are only able to determine the accuracy of $(\gamma'-\gamma'')$ and not of either γ' or γ'', so that the values given for these constants may be off by several percent.

it is known from our work to be published in a later paper that predissociation occurs at $v'=10$. All bands with $v'=10$ are diffuse in absorption and absent in emission.

The exact value of the quantum numbers K was obtained by extrapolating the Δ_2F_i curves given in Eqs. (15), (16), and (17) to $\Delta_2F_i=0$. It has thus been found that the levels with *even* K values are missing in the *lower state*, and those with *odd* K values are missing in the *upper state*.

Exactly the same results have been found in the Schumann-Runge bands of O_2 investigated by Ossenbrüggen[9] and Lochte-Holtgreven and Dieke.[10] As Mulliken[24] has shown, the normal state of the oxygen molecule is in all probability $^3\Sigma_g^-$, this being the lower state of the Schumann-Runge bands. According to the selection rules for $^3\Sigma\rightarrow{}^3\Sigma$, the upper state must then be $^3\Sigma_u^-$[10,24]. We conclude, therefore, that the S_2 here investigated are due to a $^3\Sigma_u^-\rightarrow{}^3\Sigma_g^-$ transition.

Since alternate levels are missing we conclude that the internal angular momentum of the S^{32} nucleus is zero.

Spin Fine Structure of Rotational Levels

As we have seen above, the splitting of the rotational levels of a $^3\Sigma$ state into three components is due firstly, to the interaction of the resultant electronic spin with the rotational angular momentum (see Eq. (5)), and secondly to the interaction of the individual spins of the electrons (see Eqs. (7), (8) and (9)). In the expression for the first interaction the constant γ enters and in that, for the second, the constant ϵ. As these constants have only been determined in a few band spectra, namely, O_2[20,10] and PH [25], it will be of value to determine them as accurately as possible from the data for S_2 given above.

In order to obtain the values of γ, we have to correlate Δ_2F_1, Δ_2F_2 and Δ_2F_3 given in Eqs. (15), (16) and (17) above with one of the three sets of Δ_2F values for $K\geqq 25$, Δ_2F_x, Δ_2F_y and Δ_2F_z given in Tables IV and V. By examining these Δ_2F values it is clear that γ must be small since the Δ_2F values for the same value of K are almost the same within experimental error. By averaging all the Δ_2F_x, Δ_2F_y and Δ_2F_z separately for the upper state, we find that these values can be represented by $(N-0.1)$, $(N+0.1)$ and N cm,$^{-1}$ respectively. The same result holds for the lower state. These results can now be explained by correlating the Δ_2F_z values with Δ_2F_2, and the Δ_2F_x and Δ_2F_y values with either Δ_2F_1 or Δ_2F_3 where $|\gamma'|\approx|\gamma''|\approx 0.1$. It is impossible, however, to determine definitely from our data alone whether Δ_2F_1 should be correlated with Δ_2F_x or Δ_2F_y, as we do not know whether γ is positive or negative.

It has been shown that the value of γ''[26] in the normal $^3\Sigma_g^-$ state of the O_2 molecule is negative $(=-0.025)$.[20] The value of γ'[26] for the excited $^3\Sigma_u^-$ state of the Schumann-Runge bands has also been found to be negative $(=-0.048)$.[10] We would, therefore, expect the value of γ for the normal $^3\Sigma_g^-$

[24] R. S. Mulliken, Phys. Rev. **32,** 880 (1928); **36,** 700 (1930).

[25] R. W. B. Pearse, Proc. Roy. Soc. **A129,** 328 (1930).

[26] The γ used here corresponds to $(-B)$ in Kramer's terminology (cf. ref. 20) and $(-D)$ in that of Lochte-Holtgreven and Dieke (cf. ref. 10).

and probably for the excited $^3\Sigma_u^-$ states of S_2 also to be negative.[27] Hence, if we assume γ negative Δ_2F_1 and Δ_2F_3 correspond to Δ_2F_x and Δ_2F_y, respectively, in Tables IV and V. Hence R_1(or P_1) R_3(or P_3) and R_2(or P_2) correspond to R_x (or P_x), R_y (or P_y) and R_z (or P_z), respectively, in Tables I, II and III.

A schematic drawing of the rotational levels of the S_2 molecule is given in Fig. 2, with the theoretical separation of each level from the dotted line

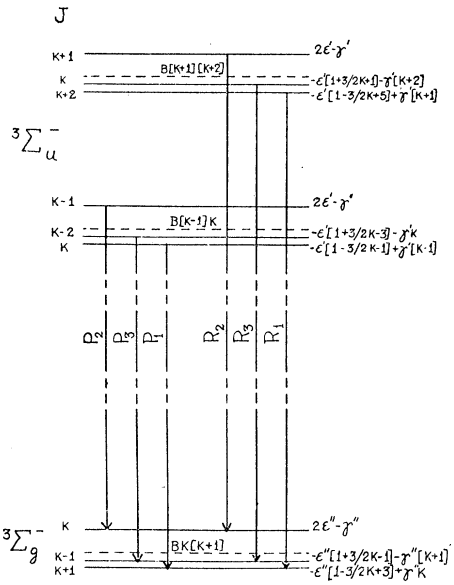

Fig. 2. A schematic representation of the structure of the rotational energy levels of S_2. The groups with rotational quantum numbers $K+1$ and $K-1$ refer to the upper $^3\Sigma_u^-$ state, and the group with quantum number K to the lower $^3\Sigma_g^-$ normal state. The dotted line represents the position of the rotational level if no interaction between K and S existed, its approximate energy value being given directly above it. The full lines represent the actual levels resulting from the interaction of the resultant electronic spin $\mathbf{S}^*$ with the rotational angular momentum $\mathbf{K}^*$ (see Eq. (5)) and the interaction between the individual spins of the electrons (see Eqs. (7), (8) and (9)). The calculated separation of these levels from the dotted line is given on the right. The lines joining the upper and the lower levels represent the observed transitions and are named accordingly. The K in the diagram is the value of K''.

for every K value given on the right. The equations for the separations of the three components in the triplet in the R and P branches, as may be seen with the help of Fig. 2, are[28]

[27] According to J. H. van Vleck (Phys. Rev. **33**, 467, 1929), $\gamma=\sum_K C_K A_K B_K/\nu_K$. The summation is to be taken over all the II states. It is likely, however, that there will be one II state whose influence is much greater than that of all others. ν_k then will be the interval between this II state and the Σ state in question. C_KA_K is the coefficient at the magnetic interaction in this II state. B has the usual meaning. We would expect this II state to be similar in O_2 and S_2. Hence the sign at γ for both molecules would in all probability be the same.

[28] The values in ϵ/K have not been omitted in these equations.

$$R_1 - R_3 = -6\epsilon'(2K + 3/4K^2 + 12K + 5) + 6\epsilon''(2K - 1/4K^2 + 4K - 3) - (3\gamma' - \gamma'') - 2(\gamma' - \gamma'')K \quad (18a)$$

$$R_2 - R_1 = (3\epsilon' - 3\epsilon'') - (3\epsilon'/2K + 5) + (3\epsilon''/2K + 3) - 2\gamma' + \gamma'' - (\gamma' - \gamma'')K \quad (19a)$$

$$R_2 - R_3 = (3\epsilon' - 3\epsilon'') + (3\epsilon'/2K + 1) - (3\epsilon''/2K - 1) + \gamma' + (\gamma' - \gamma'')K \quad (20a)$$

$$P_1 - P_3 = -6\epsilon'(2K - 2/4K^2 - 8K + 3) + 6\epsilon''(2K - 1/4K^2 + 4K - 3) + \gamma' + \gamma'' - 2(\gamma' - \gamma'')K \quad (18b)$$

$$P_2 - P_1 = (3\epsilon' - 3\epsilon'') - (3\epsilon'/2K + 1) + (3\epsilon''/2K + 3) + \gamma'' - (\gamma' - \gamma'')K \quad (19b)$$

$$P_2 - P_3 = (3\epsilon' - 3\epsilon'') + (3\epsilon'/2K - 3) - (3\epsilon''/2K - 1) - \gamma' + (\gamma' - \gamma'')K. \quad (20b)$$

The average of Eqs. (19a) and (19b) is:

$$\approx (3\epsilon' - 3\epsilon'') - (3\epsilon' - 3\epsilon'')/(2K + 3) - (\gamma' - \gamma'') - (\gamma' - \gamma'')K \quad (21)$$

and the average of Eqs. (20a) and 20b) for $K \geqq 5$:[29]

$$\approx (3\epsilon' - 3\epsilon'') + (3\epsilon' - 3\epsilon'')/(2K - 1) + (\gamma' - \gamma'')K. \quad (22)$$

The interval between R_2 and the mean of R_1 and R_3 is for $K \geqq 3$ [29]

$$3(\epsilon' - \epsilon'') + \tfrac{1}{2}(\gamma' - \gamma''). \quad (23)$$

This interval is the same as that obtained from the P branches.

Eqs. (18a) to (23) may now be used to correlate definitely the branches designated by R_x, R_y and R_z (or P_x, P_y and P_z) with R_1, R_3 and R_2 (or P_1, P_3 and P_2). The average of the experimental values $\delta\nu_R$ and $\delta\nu_P$ given in Tables I, II, and III are plotted in Fig. 3, Graph A. It is recalled that $\delta\nu_R$ and $\delta\nu_P$ are the intervals between the weak R_z (or P_z) and the corresponding strong lines R_{xy} (or P_{xy}). When the components of the strong lines become resolvable, $\delta\nu_R$ ($\delta\nu_P$) are the intervals between R_z (or P_z) and the center of the resulting doublet. The values of the average intervals between the weak lines R_z (or P_z) and the corresponding short wave-length component of the doublet R_x (or P_x), i.e. the average of $(R_z - R_x)$ and $(P_z - P_x)$ are plotted below Graph A. The values of the average intervals between the weak line R_z (or P_z) and the long wave-length component of the doublet R_y (or P_y), i.e. the average of $(R_z - R_y)$ and $(P_z - P_y)$ are plotted above graph A.

We see that the plotted values of $\delta\nu_R$ and $\delta\nu_P$ (graph A) are approximately constant, and independent of K. Further, as can be seen from Fig. 3, the average of the intervals $\delta\nu_R - (R_z - R_x)$ and $\delta\nu_P - (P_z - P_x)$ is approximately equal but of opposite sign to the intervals $\delta\nu_R - (R_z - R_y)$ and $\delta\nu_P - (P_z - P_y)$.

[29] These equations contain approximations which hold only for the values of K as given.

Considering the results obtained above by comparing the experimental values of $\Delta_2 F$ and Eqs. (15), (16) and (17) and also Fig. 3, we see that the only possible correlation (assuming γ negative) is that R_x(or P_x) corresponds to R_1, (or P_1), R_y(or P_y), to R_3, (or P_3) and R_z (or P_z), to R_2, (or P_2).

From Eq. (23) and Graph A, $3\epsilon'-3\epsilon''+\frac{1}{2}(\gamma'-\gamma'')=-1.41$ from which we obtain $\epsilon'-\epsilon''=-0.47$[30] if we put $(\gamma'-\gamma'')=0.014$ (see below).

The points below and above graph A in Fig. 3, can now best be represented by graphs B and C, respectively, which are the graphs of Eqs. (21) and (22), if we take $(3\epsilon'-3\epsilon'')=-1.42$ and $(\gamma'-\gamma'')=0.014$. We have seen above that $\gamma'\approx\gamma''\approx-0.1$ and from $(\gamma-\gamma'')=0.014$, we conclude $|\gamma''|>|\gamma'|$.

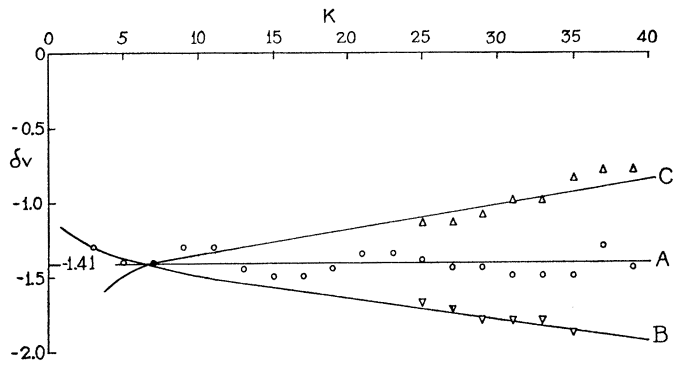

Fig. 3. Graphs showing the average observed separations of the triplets. The circular points represent the intervals between the weak R_z (or P_z) series and the strong R_{xy} (or P_{xy}) or the center of the doublets R_x and R_y (or P_x and P_y), when R_{xy} (or P_{xy}) become resolvable for $K\geqq 25$. These points are represented by Graph A. The triangles represent the intervals between the weak R_z (or P_z) series and the long wave-length component of the doublet R_y (or P_y) and the inverted triangles represents the intervals between the weak R_z (or P_z) series and the short wave-length component of the doublet R_x (or P_x). The triangles may best be represented by C which is the graph of Eq. (22), and the inverted triangles by B which is the graph of Eq. (21) where $3(\epsilon'-\epsilon'')=-1.42$ and $\gamma'-\gamma''=+0.014$. The plotted values are the averaged intervals for the R and P series.

From our data we are not able to determine the values of ϵ' and ϵ'' separately. This will be possible if the rotational structure of the S_2 bands similar to the O_2 atmospheric bands could be determined. These bands of S. which would lie in the infrared, have as yet not been discovered.

Discussion of Previous Work

With regard to previous work on the rotational analysis of S_2 there is every indication that the analysis of Henri and Teves[3] is probably incorrect, since the resolution used could not be sufficient to separate all the lines in the bands and thus to assign the lines correctly into series. The complexity of the patterns obtained in fluorescence by Teves[4], Swings,[5] and Rompe[6] are undoubtedly due to the following causes:

[30] In the O_2 Schumann-Runge bands ϵ' and ϵ'' were both found to be positive and also $\epsilon''>\epsilon'$. If we assume ϵ' and ϵ'' are also positive in the S_2 bands, then $\epsilon''>\epsilon'$.

(1) All the lines of the mercury arc have been used to excite fluorescence.

(2) As Rompe points out Swings' arc was not sufficiently cooled, giving him broad exciting lines, whereas Rompe states that he himself was unable to obtain step to step fluorescence in mercury vapour with his own source, indicating that his exciting lines were also too broad.

(3) The rotational lines of the S_2 bands lie close together.

Due to these facts and the small dispersion used by these investigators, it is extremely difficult, if not impossible, to interpret the results which have been obtained by them. It will be interesting, however, if the fluorescence spectrum could be investigated using single line excitation and somewhat larger dispersion than that used by previous investigators.

Note added in proof: We have received a letter from Mons. P. Swings in which he states that according to results derived from an investigation of the fluorescence spectra of S_2 (obtained with a Crony spectrograph with 11 prisms giving a dispersion of 1A per mm at $\lambda 3000$) he found $I''=70\times10^{-40}$ gm cm^2 corresponding to a value of $B''=0.396$ cm^{-1}. This value of B'' agrees within experimental error with our value $B_e''=0.409$ cm^{-1} given above. His results will be published in the Mém. Soc. royale Sciences, Liége.

The authors wish to express their appreciation to Professor R. S. Mulliken for his interest and advice in connection with this work.