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PERTURBATIONS AND PREDISSOCIATION IN THE S_2 BAND SPECTRUM

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Abstract

The S_2 bands belonging to the ${}^3\Sigma_u^- \leftrightarrow {}^3\Sigma_g^-$ transition have been photographed with relatively large dispersion in absorption and in emission between λ3500 and λ2400. Several perturbations have been found in the vibrational levels of the excited ${}^3\Sigma_u^-$ state. These became apparent when the quantum assignment of the band heads were determined. The following revised equation was found to fit the unperturbed heads:

$$\nu = 32250.9 + 429.5(v'+1/2) - 2.75(v'+1/2)^2 - 727.4(v''+1/2) + 2.91(v''+1/2)^2$$

Weak bands were observed (mainly in absorption) about 20 cm^{-1} to the violet of the heads in the $v''=0$ progression. These bands are believed to be due to another system. Perturbations of about $+17$ cm^{-1} have been found in the heads of the bands with $v'=0, 2, 4$, which are presumably due to perturbations of the rotational levels near the band heads by another electronic state or perturbations in the $U(r)$ curve of the ${}^3\Sigma_u^-$ state. Perturbations found in the levels with $v'>9$ are attributed to a ${}^3\Pi_u$ state which causes predissociation in these bands.

Predissociation. This phenomenon is discussed in terms of the Franck-Condon principle of transition probabilities. It is shown that the ${}^3\Pi_u$ continuous state which causes predissociation must intersect the $U(r)$ curve of the ${}^3\Sigma_u^-$ state at two points giving the two observed regions of predissociation. The relative transition probabilities for the radiationless jump in the two regions are discussed.

Dissociation. The energies of dissociation of the lower and upper states are found to be 4.45 and 2.07 volts. This gives 1.6 volts as the separation of the ${}^3P$ and ${}^1D$ states of the S atom.

I. Introduction

THE S_2 bands which extend from λ6000 to λ2300 have been studied by various investigators.[1] Rosen,[2] who gave the first quantum analysis of these bands, found that the band heads could be represented by the equation:[3]

$$\nu = 32290 + 427.1(v'+\tfrac{1}{2}) - 2.7(v'+\tfrac{1}{2})^2 - 727.4(v''+\tfrac{1}{2}) + 2.91(v''+\tfrac{1}{2})^2. \tag{1}$$

For this analysis he had a relatively small dispersion (1 mm = 300 cm^{-1} in the ultraviolet) at his disposal.

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[1] J. J. Graham, Proc. Roy. Soc. **A84,** 311 (1911); J. J. Dobbie and J. J. Fox, Proc. Roy. Soc. **A95,** 484 (1919); V. Henri and M. C. Teves, C. R. **179,** 1156 (1924); J. C. McLennan, I. Walerstein, H. G. Smith, Phil. Mag. **3,** 390 (1927); and the references given in this paper.

[2] (a) B. Rosen, Zeits. f. Physik **43,** 106 (1927); (b) ibid. **48,** 545 (1928); (c) ibid. **52,** 16 (1928).

[3] This equation is the same as that given by Rosen except that the quantum numbers have been changed from n to $(v+1/2)$.

There are large discrepancies in the combination differences[4] $\Delta G(v+\frac{1}{2})$ given by Rosen (cf. Table 15 of reference 2a) which should be the same within experimental error for any one row or column of his table. It may be concluded, therefore, either that his experimental errors were very large, which is possible since his dispersion was very small, or that the assignment of the vibrational quantum numbers to at least some of the heads, was wrong. The latter alternative is not so impossible as it may appear, since with larger dispersion in the present work it was found that many of the heads which Rosen measured as one, consist of groups of two or more heads. Furthermore, in the region above λ2900 the spectrum is so complicated due to overlapping, as can be seen from our plates, that the heads with $v' < 8$ all may have been assigned incorrectly. Therefore it became necessary for us to determine the correct assignment of the band heads before proceeding with the rotational analysis of the bands. The latter has already been published[5] and will be referred to here as I.

In the course of this investigation it was found that the irregularities in the $\Delta G(v+\frac{1}{2})$ values given by Rosen were due partly to an incorrect assignment of some of the band heads and partly to numerous perturbations in the vibrational levels of the upper state. The perturbations are larger than any that have been observed in the band systems of other molecules and therefore need special consideration.

The phenomenon of predissociation which Henri[6] found to occur in the S_2 bands, has also been studied in relation to the vibrational analysis. The interpretation of this phenomenon as it is observed in these bands differs from that given by other investigators.

II. EXPERIMENTAL PROCEDURE

Since absorption spectra obtained at different temperatures offer the best means of studying the vibrational analysis, especially of the upper electronic state, a quartz absorption cell, having a length of 5 cm and a diameter of 2.5 cm was used. The cell was first baked out and sufficient distilled sulphur was added to give a vapor pressure of 12 mm[7] at 450°C. The cell was heated electrically. Since the amount of sulphur in the cell remained constant throughout the investigation, the vapour pressure of the sulphur within the cell (above 450°C) was proportional to the temperature.

A hydrogen tube was used as continuous source.[8]

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[4] $\Delta G(v+1/2) = G(v+1) - G(v)$ where $G = E_v/hc$ (cf. R. S. Mulliken, Phys. Rev. **36,** 623, 625 (1930)).

[5] S. M. Naudé and A. Christy, Phys. Rev. **37,** 490 (1931).

[6] V. Henri, Structure des Molecules, Paris 1925; V. Henri and M. C. Teves, Nature **114,** 894 (1924).

[7] V. Henri (see Symposium of the Faraday Soc. on Molecular Spectra and Molecular Structure, Sept. 1929, p. 765) used 0.1 mg of sulphur in a 16 cc quartz tube at 600°C which gave him about the same S_2 vapour pressure.

[8] The hydrogen tube used has been described previously: S. M. Naudé, Phys. Rev. **36,** 333 (1930).

The region between λ3500 and λ2400 was studied in absorption. The absorption plates were taken with an E1 Hilger spectrograph giving a dispersion varying from 1 mm = 7.7A at λ3500 to 1 mm = 2.3A at λ2400, as well as in the first order of the 21 foot Rowland grating, giving a dispersion of 2.6A per mm. Eastman 33 plates were used. The iron and copper arcs were used as comparison spectra, the wave-lengths of which were taken from Kayser's "Hauptlinien" and Shenstone's work,[9] respectively. The copper arc was used mainly in the region below λ2800 since the iron lines are very weak and too numerous in this region to serve as standards.

The wave-lengths of the band heads on the plates obtained with the E1 spectrograph were calculated with Hartmann's formula. The measurements of the band heads obtained with both instruments agreed within experimental error. This error was relatively large (about 2 cm^{-1}), because the band heads are not very well defined owing to their characteristic rotational structure. Below λ2792.8 the heads are fuzzy due to predissociation which increases the error in this region to 5 cm.^{-1} Below λ2615 the heads become very diffuse making the experimental error as large as 10 cm.^{-1}

The S_2 spectrum was studied in emission in the region between λ3500 and λ2400. The spectrum was excited by means of a Geissler tube described in I. The plates were taken in the first order of the 21-foot grating. Iron standard wave-lengths were used as comparison spectrum.

III. DESCRIPTION OF THE PLATES

Fig. 1a is a reproduction of the bands obtained in absorption. When the absorption tube is heated to about 450°C the maximum absorption occurs in the region between λ2741 and λ2799. Plates were also taken with the absorption cell at about 600°C and 750°C. With higher temperatures the maximum absorption is shifted to longer wave-lengths as is to be expected. For temperatures of the cell below 400°C (i.e., below the boiling point of sulphur) no bands appeared in absorption in the region investigated. In emission the maximum intensity lies in the region between λ3000 and λ3500. In this region the band heads are not clearly defined owing to the great amount of overlapping. This overlapping causes many clusters of lines to be formed on the plates in this region which are not easily distinguishable from heads. These intensity relations, both in absorption and in emission, can be understood with the help of the potential energy curve obtained from the vibrational and rotational analyses given in section VII below.

Below λ2792.8 (cf. Fig. 1b) the absorption bands become diffuse. As can be seen from the plate, there are two regions in which the bands are diffuse to a different degree: first, between λ2792.8 and λ2615 and secondly between λ2615 and λ2440. The bands in the latter region are more diffuse than those in the former. In addition there seems to be a continuous absorption in the second region which reaches a maximum at λ2549. Although indications of the rotational structure reappear below λ2440 (cf. Fig. 1d) the bands are still more diffuse than in the first region.

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[9] A. G. Shenstone, Phys. Rev. **28,** 449 (1926).

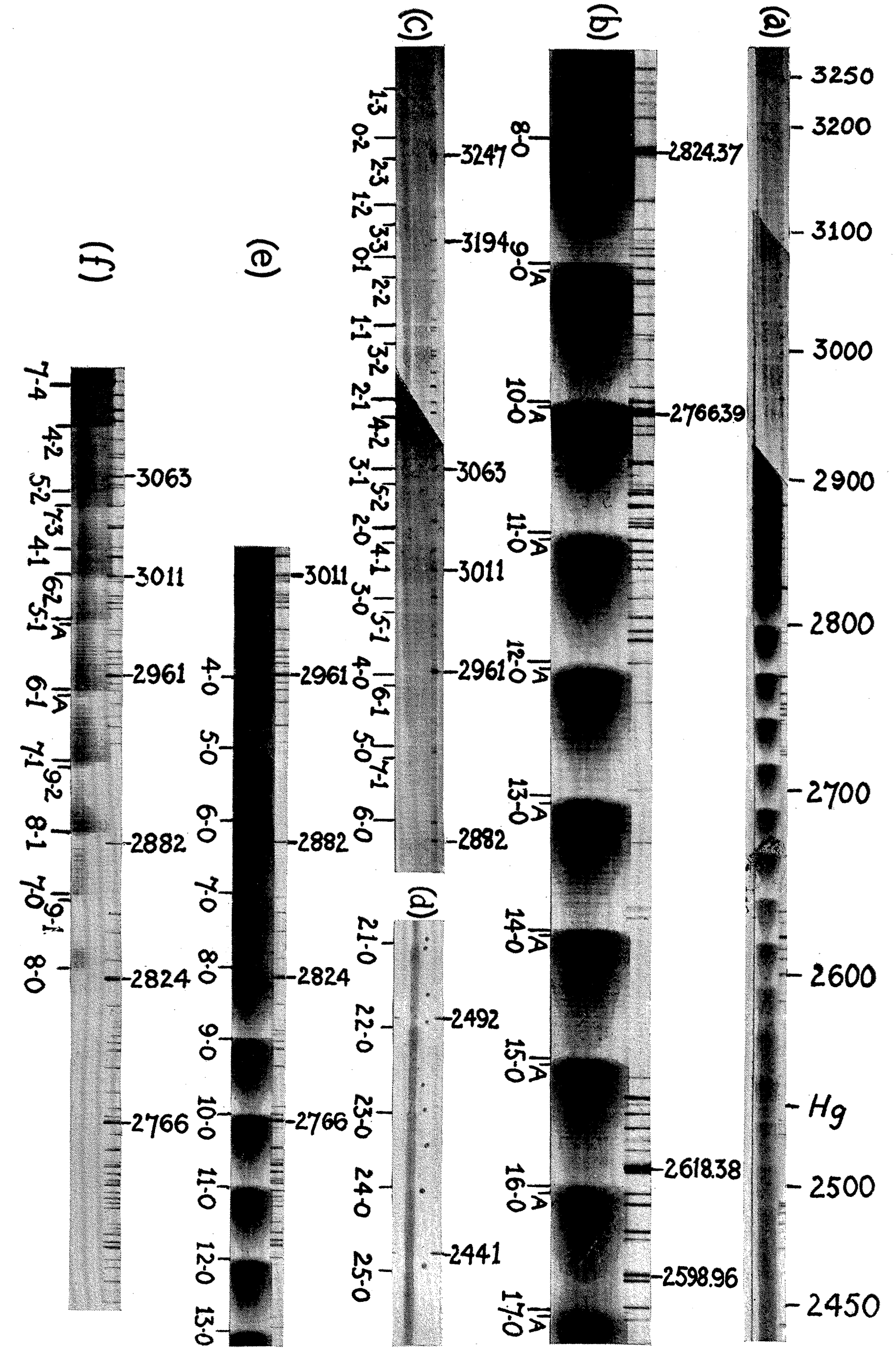

Fig. 1. (a) S_2 spectrum investigated in absorption. (b) Part of (a) showing the first region of predissociation between λ2792.8 and λ2615.0 and the first band of the second region below λ2615. (c) Absorption spectrum obtained with sulphur cell at about 750°C. (d) Bands of the second region of predissociation showing indications of rotational structure. (e) Absorption spectrum obtained with sulphur cell at about 450°C. (f) Emission spectrum of S_2.

By comparing (e) and (f) one sees that the bands which become diffuse in absorption due to predissociation do not appear in emission.

Accompanying the strong heads in absorption and about 20 cm^{-1} to the violet of these lie a number of faint heads indicated by "A" in Fig. 1b. These heads Henri and Teves[6] evidently accounted for as R heads, the strong heads being supposed to be formed by Q branches. It has been shown in I that the main system of bands is due to a ${}^3\Sigma^-{}_u \rightarrow {}^3\Sigma^-{}_g$ transition. Furthermore, the authors have found that no Q branches appear in these bands. Therefore the weak heads are probably due to a different electronic transition.

IV. THE VIBRATIONAL ANALYSIS

The band heads obtained in absorption can be arranged now as shown in Table IA. One would expect the bands which appear at the lowest temperature in absorption to correspond mainly to those having $v''=0$. Hence the band heads which were measured on the plates corresponding to the cell temperature of about 450°C can be assigned to transitions for which $v''=0$ and $v''=1$, the former being much more intense. These bands lie within zone (1) (cf. Table IA). When the temperature of the cell was raised to about 600°C, the band heads with $v''=1$ became more intense and in addition the band heads for which $v''=2$ appeared. These bands lie within zone (2). Similarly at about 750°C the bands for which $v''=3$ appear in absorption as well as a few for which $v''=4$ and 5. These bands lie within zone (3).[10,11] Most of these bands are indicated in Fig. 1c and 1e.

The consistent values of $\Delta G(v+\frac{1}{2})$ for any one column and row in Table IA prove the correctness of the assignment of vibrational quantum numbers to the various heads as brought out by changing the temperature of the absorption cell. Table IA reveals a number of irregularities in the values of $\Delta G(v'+\frac{1}{2})$ which will be discussed in section V. One would expect the $\Delta G(v'+\frac{1}{2})$ values to decrease regularly as v' increases. As is clear from Table IA, however, these values vary irregularly as v' increases.

The band heads measured on the plates taken in emission in the region λ3500 to λ2800 are given in Table IB. Most of the band heads observed in emission agree within experimental error with the absorption values. It is seen from Table IB that all the bands observed in emission have $v'<10$.

The values of the vibrational constants ω_e and $\omega_e x_e$ given by Rosen[2a] are essentially correct. He obtained the vibrational constants ω_e'' and $\omega_e''x_e''$ of the lower state from the progression having $v'=3$ which was excited in fluorescence by the mercury line $\lambda 3132\text{A}=31922$ cm.$^{-1}$. Further he derived the vibrational constants ω_e' and $\omega_e'x_e'$ for the upper state mainly from the absorption bands having $v'>4$. However, most of the heads with $v'>7$ measured by him are the weaker heads of the bands designated as A bands (cf. section III) which are discussed later. The differences between the weaker and the stronger heads are approximately constant (20 cm^{-1}) and hence the value

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[10] For the higher temperatures the absorption in the region between λ2800 and λ2600 becomes complete.

[11] By adding more sulphur to the absorption cell and increasing the temperature it would be possible to obtain the bands having $v''>4$ in absorption. This was not carried out as the above results were sufficient for our present purpose.

TABLE I. *Band heads of the* $^3\Sigma_u^- \longleftrightarrow {}^3\Sigma_g^-$ *system.*
A. Absorption

v'' / v'	0	1	2	3	4	5	Mean ΔG $(v'+\frac{1}{2})$
0		31399	30681	29974	29271	28577	
		402	407	408			405.7
1	39525	31801	31088	30382			
	433	436	435	434			434.5
2	32958	32237	31523	30816			
	400	398	396 2	393			398.3
3	33358	32635	31919	31209		3	
	422	421	422	418			421.6
4	33780	33056	32341	31627			
	384 1	385	385				384.7
5	34164	33441	32726				
	399	400					399.5
6	34563	33841			31717		
	391	388	2		392		389.5
7	34954	34233			32109		
	385	386			3		385.5
8	35339	34619					
	374	373					373.5
9	35713	34992					
	388	389					388.5
10	36101	35381					
	368	371 1					369.5
11	36472	35749					
	356	360					358.0
12	36828	36109					
	366	366					366
13	37194	36475					
	356	357					356.5
14	37550	36828					
	346						346.0
15	37896						
	333						333.0
16	38229						
	326						326.0
17	38555						
	330						330.0
18	38885						
	336	1					336.0
19	39221						
	316						316.0
20	39537	38832					
	310	303					310.0
21	39847	39135					
	292	290					292.0
22	40139						
	310	309					310.0
23	40449	39734					
	260	255					260.0
24	40709						
	301	297					301.0
25	41010	40286					
	269	268					
26	41279						269.0
		270					270.0
27		40284					
		277					277.0
28		41001					

In obtaining the mean value of $\Delta G(v'+\frac{1}{2})$, we have considered the accuracy of the measured band heads.

TABLE I. *B. Emission*

v' \ v''	0	1	2	3	4	5	6
0					29275		
					402		
1				30381	29677		
				437			
2			31527	30818			
			394	393			
3		32634	31921	31214?			29123
		422	420				
4		33056	32341	31628		30231	
		384	386				
5		33440	32727		31315		
		402	404		402		
6	34563	33842	33131		31717	31019	
	392	393			389		
7	34955	34235		32812	32106		30717
	385	383					385
8	35340	34618				31796	31102
		370					
9		34988	34269				

of ω_v derived from them is essentially correct. The dispersion used by Rosen was not sufficient to resolve these heads, and furthermore, when the vapour pressure of the sulphur in the absorption tube is increased, the weak heads become completely absorbed, and consequently one is liable to measure these as the main heads as Rosen apparently has done. This can be seen by comparing our assignment of vibrational quantum numbers to the various band heads with that of Rosen as is done in Table II. For wave-lengths greater than λ2926 the absorption spectrum becomes complicated and consequently Rosen's results become less trustworthy. In this region it is impossible to correlate our results with those given by him. Owing to these errors in Rosen's assignment the vibrational constants of the upper state as well as ν_e should be changed as follows:

TABLE II. *Comparison of assignment of vibration quantum numbers to band heads*

Present		Rosen		Present		Rosen	
$v'-v''$	ν	$v'-v''$	ν	$v'-v''$	ν	$v'-v''$	ν
7–1	34233	7–1	34237	13–0	37194	13–0	37210
6–0	34563⎫	6–0	34589	A	37214		
8–1	34619⎭			14–0	37550	14–0	37550
7–0	34954⎫	7–0	34970	A	37569		
9–1	34992⎭			15–0	37896	15–0	37900
8–0	35339	8–0	35358	A	37915		
A	35358			16–0	38229⎫	16–0	38240
9–0	35713⎫	9–0	35720	A	38247⎭		
A	35733⎭			17–0	38555	17–0	38580
10–0	36101⎫	10–0	36110	A	38885		
A	36123⎭			18–0	38885	18–0	38910
11–0	36472⎫	11–0	36480	A	38911		
A	36496⎭			19–0	39221⎫	19–0	39240
12–0	36828			A	39250⎭		
A	36851	12–0	36850				

Note: The bracketed heads have been measured as one by Rosen.

$$\nu_e = 32250.9 + 429.5(v' + \tfrac{1}{2}) - 2.75(v' + \tfrac{1}{2})^2 - 727.4(v'' + \tfrac{1}{2}) + 2.91(v'' + \tfrac{1}{2})^2. \tag{2}$$

The above mentioned faint absorption heads (cf. section III) which lie about 20 cm^{-1} to the violet of the $v''=0$ progression, have been observed only next to the main band heads having v' ranging from 8 to 20. Some of these heads are indicated by *A* in Fig. 1b. A few more weak heads have been found to appear in absorption and a few in emission which seem to belong to the same electronic transition as those marked *A*. These band heads are tabulated in Table III which gives a possible arrangement. This arrangement, however, is uncertain, since no more heads can be found, as they are relatively weak compared with the bands of the main system and are overlapped by these bands. It is therefore impossible to determine whether the upper or the lower state is common to these two systems. This might be decided in case a series of experiments were performed in which the temperature in the cell was comparatively low and the pressure was increased gradually. In addition to these two systems of bands a large number of heads have been observed above λ3500 which appear in emission. A special study of these bands, if possible with a low temperature source such as active nitrogen which would diminish the excessive overlapping of the bands, should be made in order to determine whether or not they belong to the $^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$ transition.

TABLE III. *The A System of bands of* S_2

	33476″	37214
	33879″	37569
	34269′	37908
35358	34640?	38249
35733		38577
36123		38911
36496	35794	39248
36851		39555

NOTE: (″) These band heads have been found in both emission and absorption.
(′) Found only in emission. All the other heads have been observed only in absorption.
(?) Doubtful value.

The band heads are arranged in this manner in order to show the parallelism between these heads and those of the $^3\Sigma^-{}_u \leftarrow {}^3\Sigma^-{}_g$ system.

V. PERTURBATIONS

In the great majority of band systems which have been analyzed thus far the vibrational combination difference $\Delta G(v+\frac{1}{2})$ has been found to decrease regularly as the vibrational quantum number increases.[12] If in Table IA we compare the mean $\Delta G(v'+\frac{1}{2})$ values, we see that perturbations must

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[12] It was observed by G. Nakamura in the NaH bands (Zeits. f. Physik **59**, 218 (1930)) and by T. Hori in the LiH bands (Zeits. f. Physik **62**, 352 (1930)) that the $\Delta G(v'+1/2)$ values, instead of decreasing with v', increase up to a certain value of v' and then decrease regularly. W. Weizel (Zeits. f. Physik **60**, 599 (1930)) showed that this may be accounted for by uncoupling of the $p\sigma$ and $s\sigma$ electrons.

be present in the vibrational levels of the upper $^3\Sigma^-_u$ state. This is shown more strikingly if one compares the observed and calculated energy levels as shown in Table IV. The calculated values were obtained by passing the best graph through the observed $\Delta G(v'+\frac{1}{2})$ values, and then adjusting the value of the calculated $v'=0$ level until the best fit was obtained with the experimental values. It is seen that the *o-c* values for $v'=7$ and 8 are zero within the experimental error. We know from I that the rotational levels for $v'=7$ and 8 are normal, whereas those for $v'=9$ are perturbed. From Table IV we see also that the vibrational levels $v'=7$ and 8 are normal and $v'=9$ seems to be displaced. It appears that the levels with $v'=0, 2, 4$ are perturbed by about $+17$ cm^{-1}. From $v'>9$ predissociation begins and it appears that practically all these levels are perturbed in varying degree. The perturbations for $v'=0, 2, 4$ as obtained by measuring the heads of the bands, might be due either to perturbations of the rotational lines near the heads or to perturbations of the vibrational levels.

TABLE IV. *Calculated and observed energy values of the vibrational levels for the* $^3\Sigma_u^-$ *(upper) state of the system.*

v'	*o*	*c*	*o-c*	v'	*o*	*c*	*o-c*
0	32120.0	32002.0	+18.0	12	36828.8	827.0	+ 1.8
1	32525.7	526.0	− 0.3	13	37194.8	37185.0	+ 9.8
2	32960.2	944.5	+15.7	14	37550.3	537.5	+12.8
3	33358.5	33357.5	+ 1.0	15	37896.3	884.5	+11.8
4	33780.1	765.0	+15.1	16	38229.3	38226.0	+ 3.3
5	34614.8	34167.0	− 2.2	17	38555.5	560.0	− 6.7
6	34564.3	563.5	+ 0.8	18	38885.3	890.5	− 7.2
7	34953.8	954.5	− 0.7	19	39221.3	39215.5	+ 3.6
8	35339.3	35340.0	− 0.7	20	39537.3	535.0	+ 0.3
9	35712.8	720.0	− 7.2	21	39847.3	849.0	− 1.7
10	36101.3	36094.5	+ 6.8	22	40139.3	40157.5	−18.2
11	36470.8	463.5	+ 7.3	23	40449.3	460.5	−11.2

NOTE: Our measurements below the 23←0 bands are very inaccurate, hence no comparison can be made for $v'>23$. In considering the *o-c* values it must be remembered that the experimental error for the bands having $v'<9$ is about 2 cm^{-1} and for $v'>9$ probably greater (cf. section II).

Johnson and Asundi[13] found that in the Cameron CO bands all band heads with $v'=1$ are displaced by 4.2 cm.$^{-1}$ Rosenthal and Jenkins[14] showed that all the rotational lines near the heads of these bands are perturbed, all the lines being displaced in the same direction, thus giving a displacement of the head and consequently an apparent displacement of the vibrational level. In the CN bands Rosenthal and Jenkins[15] showed that the perturbations of the rotational lines occurring in some of these bands are due to the fact that certain rotational levels of the upper state have energies approximately equal

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[13] R. C. Johnson and R. K. Asundi, Proc. Roy. Soc. **A123**, 560 (1929).

[14] J. Rosenthal and F. A. Jenkins, Proc. Nat. Acad. of Sciences **15**, 896 (1929).

[15] J. Rosenthal and F. A. Jenkins, Proc. Nat. Acad. of Sciences **15**, 382 (1929).

to the rotational levels of another state with the result that the two sets of levels are mutually perturbed, as we would expect from Kronig's theory.[16,17]

It may be that the perturbations of the S_2 band heads for $v'=0$, 1, 2, 4 are of the same type, i.e. that all the rotational lines near the band heads are displaced in the same direction and that, consequently, the heads are displaced by about $+17$ cm.$^{-1}$ But in order that the alternate vibrational levels might be perturbed, we must assume the presence of another state having an ω which is approximately twice that of the $^3\Sigma_u^-$ state. If such a state were present, we would expect transitions between this and the normal state of the molecule. It may be, however, that some of the emission bands are due to such a transition.

The observed perturbations of the band heads with $v'=0$, 2, 4 may, be due to perturbations of the vibrational levels. In this case one would expect the $U(r)$ curve to be irregular and not a smooth curve as it seems to be for the electronic states of most other molecules. A similar type of perturbation to that observed in S_2 has been found by Jevons[18] in the bands of CS, where the band heads having $v'=1, 2, 4$ were found to be displaced in the same way, the maximum displacement of the CS band heads being 7.4 cm^{-1} as compared with $+18$ cm^{-1} for S_2. Moreover, by comparing the observed displacements of the R and Q heads from their calculated positions,[19] Jevons concluded that the observed perturbations were due to perturbations of the vibrational levels.

Whether this type of perturbation as observed in the S_2 bands is due to rotational or vibrational perturbations or to a superposition of both can only be determined by studying the rotational structure of the S_2 bands having $v'=0$, 2, 4 with reference to the unperturbed bands. Owing to the great amount of overlapping of those bands in the S_2 spectrum, this study is impossible unless some other type of excitation (active nitrogen or fluorescence) will excite fewer and less extensive bands, and consequently give less overlapping. Although still difficult, this study may be carried out in the CS bands.[20]

The perturbation present in the vibrational levels for $v'>9$ may be due to the continuous state which causes predissociation and which is discussed in the next section. Although the probable error in the measurement of these diffuse bands ($v'>9$) is large (cf. section II), consequently making it difficult to interpret correctly the observed minus calculated values, it may be pointed

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[16] R. de L. Kronig, Zeits. f. Physik **50**, 347 (1928).

[17] But cf. H. H. Hyman and C. R. Jeppesen, Nature **125**, 462 (1930) and R. T. Birge and C. R. Jeppesen, Nature **125**, 463 (1930). These investigators have found a perturbation in the $v''=0$ level of the normal state of H_2, where presumably there could not be another interacting state present.

[18] W. Jevons, Proc. Roy. Soc. **A117**, 351 (1927–1928).

[19] If both the R and Q heads were displaced by the same amount, one might attribute this displacement to a perturbation of the vibrational level. If, however, the two heads were displaced by different amounts, this displacement might be due to the perturbation of the rotational levels. Cf. also references 13 and 14.

[20] This investigation has been started by one of the authors (S.M.N.).

out that, whereas the level $v'=9$ seems to be displaced downwards, those above the intersecting curve $(v'=10-16)$ seem to be displaced upwards which suggests some interaction between the corresponding $U(r)$ curves.

We know according to I from our rotational analysis of the 9–1 and 9–2 bands that the rotational levels of the $v'=9$ level are perturbed. In these bands we have found that the mean value of B_9' obtained from the Δ_2F_9' graph is larger than the B_7' and B_8'.[21] The fact that B_9' obtained from lower values of K is less than the values obtained from higher values of K (the factor $8D_vK^3$ has been considered) seems to indicate that the perturbation increases with K.

VI. PREDISSOCIATION*

It has been remarked in a previous section of this paper that there are two regions in this spectrum where the bands are diffuse. As can be seen from Fig. Ib the absorption bands are sharp[22] up to λ2799.1 $(v'=9,\ v''=0)$.[23] To the violet of this point they become at first more and more diffuse, the maximum diffuseness being at about λ2741.0 (11←0) As we proceed toward shorter wave-lengths the bands become sharper. At 2615.0 (16←0) the bands suddenly become much more diffuse, the maximum diffuseness of the second region being at λ2549.0 (19←0). From this point on the bands become less diffuse. Although the spectrum has been photographed down to λ2400, the bands below λ2492 are no sharper than those between λ2792 and λ2615, as can be seen from Fig. Id. In the first region of predissociation (λ2799–λ2615), the bands although diffuse, still preserve some of their rotational structure, the diffuse lines merging into definite groups (cf. Fig. 1b). In the second region (λ2615 – λ2435) the bands are completely diffuse, all group structure disappearing.

All the bands which are diffuse in absorption fail to appear on our emission plates (cf. Figs. 1e and 1f and also Table I).[24] No bands were observed in emission with $v'=10$, although the exposures were long enough to photograph these had their intensity been one tenth of that of the others. The non-appearance of these bands may be ascribed primarily to the small life time of the molecule in the vibrational levels of the $^3\Sigma_u^-$ state with $v'>9$, due to the transitions from these levels to those of another state with subsequent dissociation. The non-appearance of the 9→0 band may be explained by the fact that the transition probability from $v'=9$ to $v''=0$ is small. The

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[21] $B_v=B_e-\alpha_e(v+1/2)$. Hence B_v should decrease as v increases.

* The authors appreciate the discussions with Drs. J. L. Dunham and Carl Eckart about points brought up in this section.

[22] When we use the expressions: bands are "sharp" or "diffuse," we actually mean that the rotational lines of the bands are sharp or diffuse.

[23] V. Henri gave λ2792.4 as the wave-length at which the bands become diffuse (cf. reference 6). However, the band at λ2792.4 (2792.8 according to our measurements) does not belong to the main system, i.e. $^3\Sigma^- - {^3\Sigma_g^-}$, but to a weaker group of bands which are designated here as A bands and are given in Table IV. As will be shown in section VII, this wave-length has no special meaning.

[24] This fact was independently observed by H. H. van Iddekinge, Nature **125**, 858 (1930).

transition probability for $v'>9$ to $v''=0$ is still smaller, hence these bands would be weak even if predissociation was not present.

Various investigators[25,26,27] have given explanations of the predissociation, which occurs in this spectrum. Franck[25] showed that if we assume two intersecting curves as in Fig. 2A, we may expect transitions to take place at the point b with immediate dissociation of the molecule. The theoretical explanation based on wave mechanics, as given by Kronig[26] involves the same basic principles as those used by Franck. Kronig showed that the selection rules for radiationless transitions are $\Delta\Lambda=\pm 1, 0$; $\Delta\Sigma$ or $\Delta S=0$; $\Delta J=0$; and that transition can occur only between two $+$(or$-$) rotational levels belonging to two electronic states that are both g or both u.[28] [It may be pointed out that the ordinary transition rules are $\Delta\Lambda=\pm 1, 0$; $\Delta\Sigma$ or $\Delta S=0$; $\Delta J=0, \pm 1$; $+$(or$-$) levels to $-$(or$+$) levels and g(or u) to u(or g) states (if equal atoms)]. The probability of a radiationless transition is proportional to $J^2/(E)^{1/2}$.[29] E is the energy difference between any level of the $^3\Sigma_u^-$ state and the line $b\ b'$, b' being the dissociation energy of state a. The above formula would indicate that no transition is possible between the two intersecting curves below b. Hence we would expect predissociation to begin sharply and then decrease gradually as we reach the vibrational levels above the point b. However, in both the first and second region, predissociation begins suddenly and increases gradually to a maximum before it decreases.

The explanation given by Herzberg[27] for the observed predissociation in the S_2 bands is a further development of Franck's principle. According to Herzberg curve a[30] cuts the $^3\Sigma_u^-$ curve at two points, c and b, as in Fig. 2B, corresponding to the two regions of predissociation. He points out that the bands of the second region may be more diffuse, first because in this region the bands will be overlapped by the continuum[31] due to $^3\Sigma_g^- \leftarrow a$, and secondly, because at c the probability of predissociation will be greater, for at

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[25] J. Franck and H. Sponer, Nachricht Gesellschaft d. Wiss. Göttingen, Math.-Phys. Klasse, p. 241 (1928); K. F. Bonhoeffer and L. Farkas, Zeits. Phys. Chem. **134,** 337 (1927).

[26] R. de L. Kronig, Zeits. f. Physik **50**, 347 (1928); **62,** 300 (1930).

[27] G. Herzberg, Zeits. f. Physik **61,** 604 (1930).

[28] The last rule as formulated by Kronig (cf. Zeits. f. Physik **62,** 300 (1930)) is symmetrical to symmetrical, and antisymmetrical to antisymmetrical states. The $+$ and the $-$ levels here referred to are the "gerade" (g) and "ungerade" (u) rotational levels of Kronig (cf. Zeits. f. Physik **50,** 351 (1928)) and Mulliken (cf. Phys. Rev. **36,** 617 (1930). The g and u used here refer to the "gerade" and "ungerade" electronic states of Hund as Π_u, Σ_g, Σ_u, etc. (cf. Zeits. f. Physik **51,** 759 (1928)).

[29] The J^2 term in Kronig's formula enters only when the transition involves $\Delta\Lambda=\pm 1$. For a transition for which $\Delta\Lambda=0$, the probability is independent of J. The dependence on J would indicate that within any diffuse band, the rotational lines would become more diffuse as we go away from the origin. The probability essentially depends upon J and not on J^2 since $J^2/(E)^{1/2} \propto J$. It is difficult to determine from our results whether or not the lines within a band become more diffuse as we go away from the origin.

[30] Herzberg points out that curve a may or may not have a minimum. His explanation fits either case equally well.

[31] Fig. 3 shows that the most probable transition from the lower vibrational levels of the $^3\Sigma_g^-$ state is to the left of the upper curves.

this point the radiationless transition may occur before it is necessary for the molecule to complete half a vibration as it would at point *b*. It is highly improbable, however, that the overlapping continuum will make the bands appear more diffuse than they actually are. Furthermore, since the frequency of vibration is much larger than that of rotation, the fact that the molecule will have to complete half a vibration at *b* and not at *c* before it dissociates, can have no appreciable effect on the relative probability of predissociation of the bands in the two regions.

The first idea which suggests itself is that there may be two curves intersecting the $^3\Sigma_u^-$ curve, giving the two regions of predissociation. It may be well, therefore, to consider here the various possible states which may be present. It has been shown by us[5] that the main system of bands which show predissociation is due to a $^3\Sigma_u^- \leftarrow {}^3\Sigma_g^-$ transition, $^3\Sigma_g^-$ being the lower state. By a comparison with the Schumann-Runge bands of O_2 (cf. also section VII), one would expect the $^3\Sigma_g^-$ of S_2 to dissociate into two ^3P atoms, and the excited state, $^3\Sigma_u^-$, into one ^3P and one ^1D atom. It is evident also from the $U(r)$ curves that the states which cause predissociation must dissociate into two normal atoms. By applying the results of Wigner and Witmer,[32] one finds that the molecular electronic states resulting from similar atoms both in a ^3P state are the following: $^1\Delta_g$, $^1\Pi_g$, $^1\Pi_u$, $^1\Sigma_g$, $^1\Sigma_g^-$, $^1\Sigma_u^-$, $^3\Delta_u$, $^3\Pi_u$, $^3\Pi_g$, $^3\Sigma_u^+$, $^3\Sigma_u^+$, $^3\Sigma_g^-$, $^5\Delta_g$, $^5\Pi_g$, $^5\Pi_u$, $^5\Sigma_g^+$, $^5\Sigma_g^+$, $^5\Sigma_u^-$. The state or states causing predissociation (curve *a* in Fig. 2B or Fig. 2C) must be among the above. But according to the rules given by Kronig[16] for a radiationless transition, the only state in the above list which can interact with a $^3\Sigma_u^-$ state is a $^3\Pi_u$ state. Hence the state which causes predissociation must be a $^3\Pi_u$ state and must intersect the $^3\Sigma_u^-$ at two points as Herzberg assumed.[27] However, we have still to explain why the bands in the second region corresponding to *c* are more diffuse than those in the first.

It may be shown that Kronig's formula does not apply to the region *c*. In deriving his formula,[33] he assumed that the nuclear momentum of the molecule in state *a* (here identified as a $^3\Pi_u$ state) is constant. That is, he was dealing only with the flat portion of the curve, line *b b′* of Fig. 2A. If, however, the curve has no minimum[34] as in Fig. 2C the momentum will not be constant near either of the points *b* or *c*.[35]

[32] E. Wigner and E. E. Witmer, Zeits. f. Physik **51**, 859 (1928).

[33] Kronig took as the wave function of state *a* an oscillatory function with a constant period, i.e., constant momentum.

[34] The $^3\Pi_u$ state may have a very shallow minimum. If it had a sharp minimum we would expect to find discrete bands either in emission or absorption due to a $^3\Pi_u \longleftrightarrow {}^3\Sigma^-_g$ transition. No such bands have been found although there is a region of weak continuous absorption beginning at about λ2600 which may be ascribed to this transition. The group of bands designated in this paper as *A* bands are not due to this transition, for they are found in absorption after the point *c* has been passed.

[35] Since the $^3\Pi_u$ intersects the $^3\Sigma_g^-$ curve at *c*, we will have to suppose that although the interaction between the two atoms forming the $^3\Pi_u$ state is almost zero for very small distances of internuclear separation, when this distance is made still smaller, the repulsion between the two atoms is smaller than that in state $^3\Sigma_u^-$. (This will be the case if the electronic configuration of the $^3\Pi_u$ state resembles the united atom more closely than that of the $^3\Sigma_u^-$ state.)

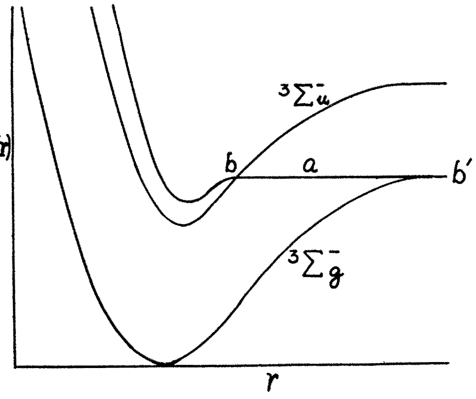

Fig. 2A

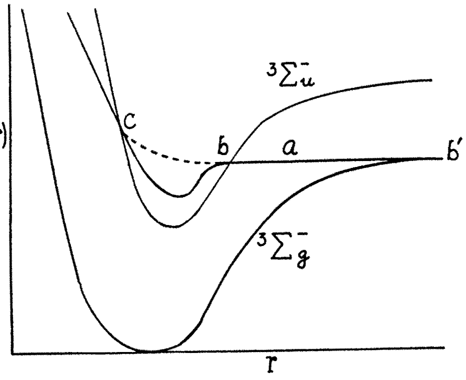

Fig. 2B

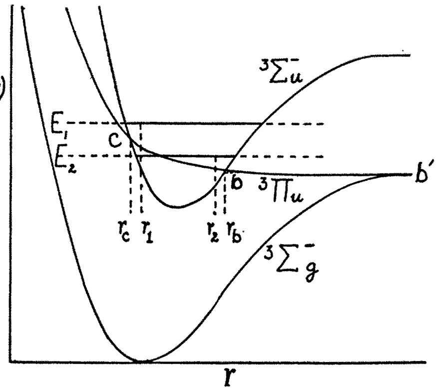

Fig. 2C

In the tentative explanation given here we shall make use of the Franck-Condon theory[36] of transition probabilities between the two states $^3\Sigma_u^-$ and $^3\Pi_u$. According to this theory the probability of a transition is greatest when

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[36] E. U. Condon, Phys. Rev. **28**, 1182 (1926).

the nuclear separation as well as the momentum remain unchanged during the transition. Since the slopes of the two intersecting curves are more nearly alike at the point c than at b, and furthermore remain closer together at the former point than at the latter, a transition from a discrete vibrational level whose energy is near that of c to the continous curve will involve a very much smaller change in the nuclear separation at this point than at the point b. The ratio of the nuclear momenta in the neighbourhood of the two points is approximately the same in both cases. This can be seen from Fig. 2C. If we take two discrete vibrational levels E_1 and E_2 so that $E_1-c=E_2-b$, and consider the points on E_1 and E_2 having zero nuclear momentum it is quite evident that the difference of the nuclear separation for the former is much less than for the latter. For two other points on E_1 and E_2 having nuclear separations r_1 and r_2 so that $r_1-r_c=r_b-r_2$ the ratios of the nuclear momenta in the former case will be about the same as in the latter. Hence the probability of the predissociation at the former point will be greater (therefore the rotational lines more diffuse) than at the latter point. Furthermore, since the two curves remain closer together near c, i.e. the second region of predissociation, we would expect more bands to be diffuse in the second region of predissociation than in the first. Finally, from the above explanation we would expect that, in both regions of predissociation, the bands tend to become more diffuse as we approach the points of intersection from either side.[37] These phenomena are exactly what we observed.

It has been stated in a previous section that the overlapping continuum reaches a maximum at λ2549. This maximum could not be due entirely to transitions between the $^3\Sigma_g^-$ and the $^3\Pi_u$ states, for according to Fig. 3, the maximum probability of this transition should occur at λ2662. We have also seen that the band at λ2549 ($19\leftarrow 0$) is the most diffuse band in this spectrum. Hence the overlapping continuum at this point must be due to the fact that the rotational levels for the $v'=19$ are so diffuse as to be practically continuous.

For a quantum mechanical formulation of the results obtained by application of the Franck-Condon principle, we would make the step by step conversion from one to the other exactly as Condon has done for ordinary transitions.[38] One sees that the overlapping of the wave functions of the two states ($^3\Sigma_u^-$ and $^3\Pi_u$) is greater at c than at b since the internuclear distances (with zero nuclear momentum) on both curves are nearer the same in the neighborhood of the former point than of the latter. Therefore the two waves will tend to reenforce each other more at c than at b, giving a greater transition probability in the neighborhood of c.

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[37] L. A. Turner (Am. Phys. Soc. Meeting, New York, Feb. 1931, Paper No. 12) refers to two types of predissociation. In one the broadening of the lines sets in suddenly at a definite wavelength and in the other it sets in gradually. The former is the type discussed by Kronig (cf. Fig. 2A) and is also approximated at point b of Fig. 2C. According to our interpretation the continuous curve at point b has almost the value of dissociation. Hence at this point one would expect the broadening of the lines to set in more suddenly than at point c.

[38] E. U. Condon, Phys. Rev. **32,** 858 (1928), also Condon and Morse, Quantum Mechanics, pp. 168–170.

In the above discussion we were concerned mainly with the $^3\Sigma_u^- \longleftrightarrow {}^3\Sigma_g^-$ bands. The other system of bands which we have designated as *A* bands shows exactly similar characteristics. Whenever a band of the main system is diffuse the corresponding *A* band is also diffuse.

While this paper was being written Asundi[39] reported that in the presence of argon at high pressures, he was able to photograph the bands in emission beyond the first limit of predissociation. If the mechanism of predissociation given by all thus far is correct, it is difficult to see what effect the presence of argon could have except that of increasing the population of the levels with $v'>9$. Thus, although dissociation does take place there are still sufficient molecules present in these states to emit the bands with sufficient intensity to be observed.

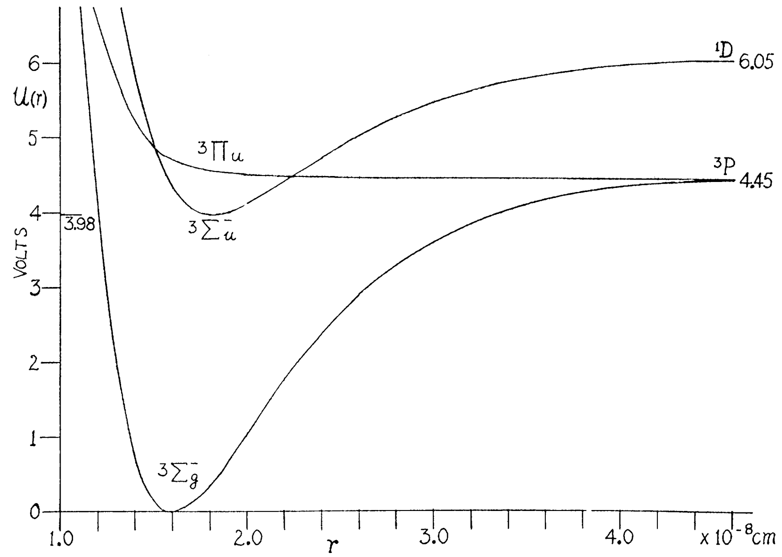

Fig. 3. Potential energy curves of the known states of the S_2 molecule. The $^3\Sigma^-_g$ and $^3\Sigma^-_u$ curves have been drawn using Morse's equation.

VII. Heats of Dissociation

In our previous paper[5] we showed that the main system of S_2 bands is due to a $^3\Sigma_u^- \longleftrightarrow {}^3\Sigma_g^-$ transition, and is analogous to the Schumann-Runge bands of O_2. We should, therefore, expect the normal $^3\Sigma_g^-$ state of S_2 to dissociate into two ^3P atoms just as in the case of O_2, and similarly the upper state $^3\Sigma_u^-$ to dissociate into a ^3P and a ^1D atom.

From the graph $\omega_v{:}v$ for the $^3\Sigma_u^-$ state we obtain by linear extrapolation 2.07 volts for the heat of dissociation D' of this state.[40] Hence the total energy required to excite the molecule into the $^3\Sigma_u^-$ state and to dissociate it is:

$$\nu_e + D' = 3.98 + 2.07 = 6.05 \text{ volts.}$$

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[39] R. K. Asundi, Nature **127**, 93 (1931).

[40] Of the 2.07 volts the energy is known up to 1.01 volts and the rest is extrapolated.

The $^3\Pi_u$ level which causes the predissociation must also dissociate into two ^3P atoms, since there is no other possible atomic state between the ^3P and ^1D states. From the description of the phenomenon of predissociation as observed in these bands given in section VI it is clear that the rotational lines of the bands, are sharp up to λ2792.8 where they begin to become diffuse. The rotational lines immediately below λ2792.8 which are diffuse in absorption correspond to transitions from the higher rotational levels in $v''=0$ to the corresponding levels of $v'=10$. These lines are diffuse because the rotational levels of $v'=10$ have energies which lie in the continuous energy range of the $^3\Pi_u$ curve (i.e. $>D''$). Since the lines near the head of the 10–0 band ($\nu=36101$ cm^{-1}) also are diffuse the energies of these lines are greater than D''. The head of the 9–0 band is sharp so that its energy is less than D''. In I, moreover, it was shown that the rotational lines of the 9–1 and 9–2 bands could be followed to $K\approx 30$. The line having $K\approx 30$ corresponds to an energy $35713\ \text{cm}^{-1}+B_9K(K+1)\approx 36000\ \text{cm}^{-1}$. This energy must be less than D'' otherwise the rotational lines could not have been observed in emission. D'' must therefore lie between 36000 and 36100 cm.$^{-1}$ Therefore $D''=4.45\pm 0.01$ volts.[41] This value is in good agreement with the chemical value 103600 cal $=4.5$ volt obtained by Budde.[42] By extrapolation of th $\omega_v{:}v$ graph for the $^3\Sigma_g^-$ state we ought to obtain the same value for its energy of dissociation D''. But, as in the case of O_2, this extrapolation leads to a value of D'' which lies above the correct values for S_2 as obtained from predissociation.[43]

Using the values of r_e' and r_e'' given in I and the values of ν_e, D' and D'' obtained above, we are able to draw the potential energy curves of the $^3\Sigma_g^-$ and $^3\Sigma_u^-$ states of S_2 using Morse's equation,[44] (see Fig. 3). Assuming the $^3\Pi_u$ curve to intersect the $^3\Sigma^-{}_u$ curve at about $v'=19$ and $v'=11$ according to section VI and to give two ^3P atoms, we may draw this curve as shown in Fig. 3.

According to the above results the separation of the ^1D and ^3P atomic states must be $6.05-4.45=1.60$ volts. The value of this separation for O as given by Frerichs[45] is 1.95 volt and the corresponding separations in the Se and Te atoms as determined by McLennan and Crawford[46] are 1.2 and 1.3 volts. By interpolating we obtain 1.6 ± 0.1 volts for S which is in good agreement with the value given above;

The authors wish to thank Professor R. S. Mulliken for his interest and criticism in connection with this work.

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[41] G. Herzberg, Zeits. f. Physik **61,** 604 (1930) lays great stress on the fact that one can obtain only a maximum value of the energy of dissociation from predissociation data. From our interpretation of the phenomenon it is clear that a fairly accurate determination is possible for S_2.

[42] Budde, Zeits. f. Analyt. Chem. **78,** 169 (1912).

[43] The linear extrapolation in this case will be very inaccurate as it is much greater than in the $^3\Sigma_u^-$ state.

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

[45] R. Frerichs, Phys. Rev. **36,** 398 (1930).

[46] J. C. McLennan and M. F. Crawford, Nature **124,** 874 (1929).

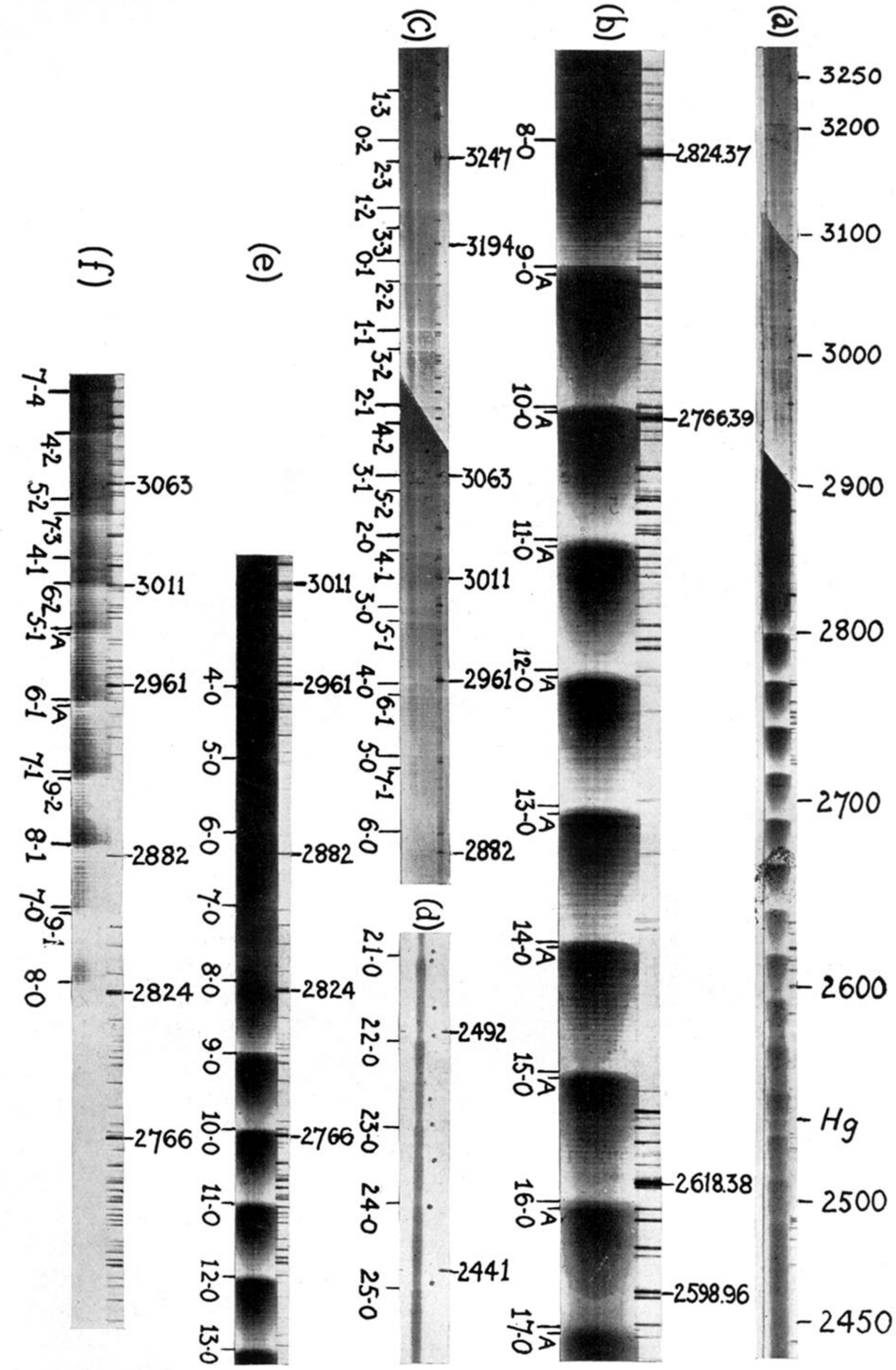

Fig. 1. (a) S_2 spectrum investigated in absorption. (b) Part of (a) showing the first region of predissociation between λ2792.8 and λ2615.0 and the first band of the second region below λ2615. (c) Absorption spectrum obtained with sulphur cell at about 750°C. (d) Bands of the second region of predissociation showing indications of rotational structure. (e) Absorption spectrum obtained with sulphur cell at about 450°C. (f) Emission spectrum of S_2.

By comparing (e) and (f) one sees that the bands which become diffuse in absorption due to predissociation do not appear in emission.