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Publication Date
1957-02-01

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ABSTRACT

A search was made for the absorption spectrum of the SO molecule corresponding to the emission spectrum assigned to this molecule by Henri and Wolff.[2] Spectrograms were taken under thermal equilibrium conditions with a wide variety of SO_2 and S_2 pressures, but no trace of the SO absorption spectrum was found. However, the heat of formation of SO measured by St. Pierre and Chipman[7a] is strong evidence that the lower state of the emission system is the ground state of the SO molecule. A re-evaluation of their data leads to values for D_0 of SO and S_2 of 5.027 ± 0.050 and 3.3 ev respectively.

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INTRODUCTION

The emission spectrum of the SO molecule was first observed by Lowater in 1906 in a discharge through SO_2 gas.[1] She described bands appearing at from 2400 to 4000 A, but did not establish the true carrier of the band system. In 1929 Henri and Wolff made a vibrational analysis of this band system and attributed the transition to the diatomic SO molecule.[2] The system was analyzed under higher dispersion by Martin, who determined that the upper and lower states of the transition were of the $^3\Sigma$ type and obtained rotational constants for these two states.[3] Furthermore, Martin noticed a breaking off of the emission spectrum of this molecule at the $v' = 3$, $K' = 6$ level of the upper state of SO. If one assumes that the lower state of this transition is the ground state of the SO molecule, then from this predissociation limit one may arrive at two possible values for the heat of dissociation of the SO molecule at $0°K$, D_0; these arise because of ambiguity in the dissociation products of the repulsive state responsible for the predissociation.

There are two ways in which one might prove that the lower state of this transition is the ground state of SO. One method would be an accurate thermochemical measurement of the heat of formation of SO; if the measured value corresponded closely with one of the possible dissociation energies of SO, then the lower $^3\Sigma$ state would be proven to be the ground state or at least close to it. Such a measurement has been made by St. Pierre and Chipman,[7a] and their results indicate that the lower state of Henri and Wolff's transition probably is the ground state of SO. This work is discussed in detail in Appendix A. A more direct method of proving that the $^3\Sigma$ state is the ground state of SO would be to find the absorption spectrum of the above-mentioned transition under conditions such that no excited state could have an appreciable population.

As yet no absorption spectrum has been observed for the SO molecule. In 1933 Cordes and Schenk reported an absorption spectrum appearing in the region 2500 to 3400 A when they passed a discharge through SO_2 gas and sulfur.[4] An analysis of their discharge products showed a one-to-one molar ratio of sulfur to oxygen. A linear extrapolation of the upper state of their transition led to Martin's dissociation energy for SO. Thus they attributed the absorption spectrum to the SO molecule.

However Kondrat'eva and Kondrat'ev took issue with the assignment of the absorption spectrum to this molecule.[5] They were able to produce the absorption spectrum under conditions in which they considered the formation of SO to be energetically impossible. In addition they decided that the absorption spectrum was too complicated to be produced by a diatomic molecule and suggested S_2O_2 as the source of spectrum. Support for this conclusion is found in the more recent investigation by Jones,[6] who produced Cordes and Schenk's absorption spectrum in a manner similar to theirs. Furthermore he found a vibrational frequency in the infrared region of the discharge spectrum 679 cm^{-1}, which also appeared in the ultraviolet absorption spectrum. He ruled out the possibility that the ultraviolet and infrared transitions were produced by the SO molecule, since the rotational and vibrational constants found by Henri, Wolff, and Martin were not found in the infrared spectrum. Also more than one vibrational frequency was found in the infrared region. He also suggested that the carrier of the ultraviolet and infrared band systems might be S_2O_2.

The most recent investigation of the ultraviolet and infrared absorption spectra indicates that their carrier is the S_2O molecule. Meschi and Myers, on the basis of mass spectrometric, stoichiometric, and effusion measurements, found that the products of a discharge through SO_2 and sulfur vapor were equimolar quantities of S_2O and SO_2.[7] They explained the equal quantities of these two molecules produced on the basis that they are the final products of the decomposition of SO, which might be the major but temporary species in the effectively high temperatures of the discharge. They then attributed the 1165- and 679-cm^{-1} absorption bands of the infrared absorption to the S-O and S-S stretching frequencies of the S_2O molecule.

The purpose of the investigation here reported was to produce the true absorption spectrum of the SO molecule corresponding to the emission spectrum first found by Lowater. If the SO molecules were produced in an equilibrium thermal source at comparatively low temperatures, then the discovery of such an absorption spectrum would be strong evidence that the lower state of the transition is the ground state of the SO molecule.

PRELIMINARY CALCULATIONS
Band-Head Locations of SO and Related Molecules

From the tabulated band head locations and estimated intensities presented by Henri and Wolff[2] for the emission band system of SO, one may calculate the location of the strongest band heads of this system in absorption. The intensities of the different vibrational bands in absorption were estimated from the emission intensities by the use of the Boltzmann factor and the Franck-Condom principle. Table I gives the location of the band heads that should appear strong in absorption; the strongest of these should be the (3-0) band. In emission the (3-0) band appears broken off at $K' = 6$ and the (4-0) band does not appear at all, owing to a predissociation noted by Martin.[3] However, in absorption these bands should appear, although they may be diffuse in nature.

Table I

The locations of the strongest absorption band-heads of SO along with strong bands of the S_2 molecule that might overlap. All bands are degraded to the violet.

| SO molecule		S$_2$ molecule [a]			
v',v''	$\lambda(A)$	v',v''	$\lambda(A)$	v',v''	$\lambda(A)$
1,1	2589.0	17,0	2615.0	23,0	2490.6
2,1	2548.6	18,0	2592.9	24,0	2471.6
1,0	2516.4	19,0	2570.9	25,0	2455.7
2,0	2477.7	20,0	2548.9	26,0	2437.7
3,0	2442.0	21,0	2528.5	27,0	2421.8
4,0	2408.3[b]	22,0	2508.8	28,0	2404

[a]Band head locations obtained from Rosen.[8]

[b]Position calculated from the vibrational data of Henri and Wolff.[2]

In any method by which SO is produced at moderate temperatures (1000°C), appreciable concentrations of S_2 or SO_2 gas are present. Both these molecules have strong absorption spectra in the region where one may expect to find strong SO absorption bands. In Table I are presented the locations of strong S_2 absorption bands that might interfere with the finding of the SO absorption bands. The possible SO_2 absorption bands occurring in this region are too numerous to list here. The location of such bands may be calculated from the data of several workers;[9, 10, 11, 12] these bands are degraded to the violet, as are those of S_2 and SO. In the region of 2400 to 2600 A the S_2 absorption spectrum is diffuse, and thus appreciable concentrations of S_2 prevent the observation of the SO spectrum.

Thermodynamics of the SO Molecule

In order to have the optimum chance of observing the SO spectrum, we may predict the conditions under which one obtains the greatest pressure of SO relative to that of S_2 or SO_2. For this purpose let us consider the reaction

$$SO_2(g) + 1/2\ S_2\ (g) = 2\ SO\ (g). \tag{1}$$
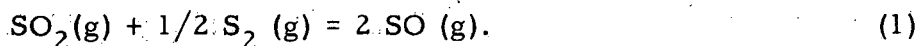
At 298°K the heat of formation of SO_2 gas from S_2 gas and O_2 gas is -86.37 kcal per mole;[13] for SO gas it is -18.9 kcal per mole. (See Appendix A) Thus the heat of Reaction (1) at 298°K is +48.6 kcal per mole. Now if we consider that $\Delta F^\circ/T = \Delta H^\circ/T - \Delta S^\circ$, we may see that SO becomes more stable with increasing temperature. Unfortunately the equipment in this experiment did not allow observation of the above system at temperatures higher than 1273°K.

At this temperature one may calculate the equilibrium constant for Reaction (1) by using the $(F^\circ - H^\circ_{298})/T$ values for the different species given by Kelley[14] in conjunction with the heat given for the reaction above. Thus one calculates $K = 1.10 \times 10^{-4}$ at 1273°K when the pressures of the various species of Reaction (1) are given in atmospheres. By using this equilibrium constant one may calculate the pressure of SO gas produced when different pressures of S_2 and SO_2 are used.

Using these thermodynamics, we may check the hypothesis of Meschi and Myers that in the high effective temperature of an electrical discharge the reaction of sulfur and SO_2 is virtually complete to form SO.[7] This time we must consider the reaction

$$SO_2(g) + S\ (g) = 2\ SO\ (g), \tag{2}$$

since most of the sulfur vapor will be monatomic at these temperatures (see Appendix B). Using the free energies of Kelley and a heat for Reaction (2) at $298^{\circ}K$ of +10.1 kcal per mole, we arrive at an equilibrium constant of 3.2 at a temperature of $3000^{\circ}K$. Thus even at this temperature the sulfur will be mainly in the form of SO; at the probably higher effective temperatures of the discharge we might expect virtually complete formation of SO. In the cooler parts of the discharge tube this would break down into equimolar quantities of S_2O and SO_2. Thus since excess sulfur would immediately condense at room temperature one would collect only the S_2O and SO_2 in a cold trap and thus obtain the one to one ratio of sulfur to oxygen found by Schenk.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Dr. Karl Wieland originally constructed the furnace used to produce the temperatures needed in this experiment. The furnace consisted of a porcelain tube approximately 100 cm long and 8 cm in inside diameter. The tube was wound with No. 15 gauge nichrome wire in three separate coils, so that the amount of power dissipated at the ends of the tube could be varied with respect to the middle of the tube. The porcelain tube and windings rested inside a cylinder of sheet aluminum; magnesium oxide and asbestos insulation was packed between the windings and the aluminum cylinder. Quartz windows helped to prevent convection heat losses out of the ends of the porcelain tube.

The three coils were connected in parallel to a Powerstat which in turn was connected to a 220-volt line. A power input of less than 6 kva produced a temperature above $1000^{\circ}C$; operation of the furnace at temperatures higher than this for appreciable periods of time would have damaged the nichrome windings. The temperatures were measured by means of a chromed-alumel thermocouple.

The gases to be studied were contained in a quartz cell resting on the inside of the porcelain tube. The cylindrical cell was 50 cm in length and 5 cm in diameter; polished plate quartz 2.4 mm thick was used for the two end windows of the cell. The sulfur pressures were controlled by the use of

a side arm which projected from the end of the furnace and was also wound
with nichrome wire so that its temperature could be controlled separately
from the furnace. The pressure of the S_2 vapor could be calculated by
knowing the vapor pressure of the S_8 over the solid sulfur at a particular
temperature in the side arm. Stull and Sinke tabulate free energy functions
for S_8.[15]

In some instances the sulfur pressure was determined by inserting
a small quantity of a very dilute solution of sulfur in cyclohexane into the
cell and sealing off the side arm so that it was entirely within the furnace.
The oxygen pressure in the cell was controlled by sealing off the side arm
under different pressures of air as measured by a calibrated Pirani gauge,
high-pressure McLeod gauge (100 to 750 μ of mercury), and a mercury
manometer in the appropriate pressure ranges.

The sulfur atmosphere reacted with the quartz cell and left an
opaque deposit on the window of the cell at the elevated temperatures of the
experiment. This phenomenon was not caused by transport of Si due to the
formation of SiO or SiS molecules; at 1300°K these species are unimportant.
Possibly a polyatomic molecule of Si and S was responsible for the transport.
The opaque deposit made longer exposures necessary; consequently the
windows of the cell were replaced periodically.

Most of the observations were made with a small quartz prism
spectrograph having a dispersion of approximately 24 A per mm at 2450 A.
At slit widths of 0.1 mm, exposure times of the order of several minutes
were used, according to the particular conditions of the observation. A
scale built into the spectrograph was photographically printed on each plate.
The strong Hg 2537 A line, which appeared in both of the continuous sources,
provided a means of obtaining the scale correction. When conditions of
special interest were noted by use of the small spectrograph, the spectra
were examined by means of a 21-foot grating spectrograph which yielded
a dispersion of 1.24 A per mm at 2450 A. With slits set at 0.035 mm, ex-
posure times as long as one or two hours had to be used. The plates were
calibrated by means of iron arc.

Eastman Kodak IIaO, 103aO, and 103-O spectroscopic plates provided
suitable sensitivity in the wavelength region of interest. The plates used on
the 21-foot grating spectrograph were long enough to cover a region of

several hundred Angstroms. Some of the plates were developed as long as 15 minutes in D-19 developer to bring out maximum contrast.

Two sources were used to produce the strong ultraviolet continuum needed for this search. One was a high-pressure xenon compact arc lamp; this lamp emitted a great deal of light in the visible region of the spectrum as well as the ultraviolet continuum. This property of the source caused a great deal of difficulty, for in either spectrograph the scattered visible light was almost as intense as the ultraviolet continuum at 2500 A. This situation was slightly alleviated by the use of a filter consisting of a solution of $CoSO_4$. The solution had a concentration of 70 g $CoSO_4 \cdot 7H_2O$ per liter of water, and a path length of 1 cm was used. Such a filter gives about 80% transmission at 2500 A, but absorbs most of the light at 5000 A.[16]

Some improvement was achieved through the use of a hydrogen discharge lamp. The lamp was operated at 1000 volts with a current of about 1 ampere; the hydrogen pressure was 2 mm. Such a lamp provides an ultraviolet continuum of about the same intensity as the xenon lamp, but emits relatively less visible light.

The chance of finding the SO absorption spectrum increases if longer path lengths of the absorbing gas are used. Longer path lengths would enable one to observe the spectrum with smaller concentrations of SO. This is an advantage, since at lower pressures the ratio of SO to S_2 or SO_2 is greater. For this purpose an attempt was made to reflect the light from the source so that it made several traversals through the absorption cell before reaching the spectrograph. A suitable system of mirrors was available for this purpose; Wieland had constructed such a system similar to that built and described by Bernstein and Herzberg.[17] Unfortunately it was found that even though the front surface of the mirrors had been silvered, the mirrors reflected considerably more light in the visible than in the ultraviolet region of the spectrum. This resulted in greatly magnifying the problem of scattered light; as a result even when only two traversals through the absorption cell were used, little intensity could be observed below 2500 A. Thus the results presented in the next section were obtained by using only one traversal of the absorption cell.

RESULTS

The final procedure adopted then in making the search was to seal air in the quartz cell at a certain pressure, and then take spectrograms while varying the sulfur pressure. Then the cell was broken open again and resealed with a different air pressure. Thus the spectrograms covered a wide range of sulfur and oxygen pressures. The results of the search are summarized in Table II.

Table II

Results of spectrograms taken at different pressures of oxygen and sulfur. In all cases the temperature of the gases was $1273^\circ K$.

SO_2 pressure (atmos x 10^6)	S_2 pressure (atmos x 10^6)	SO pressure (atmos x 10^6)	Observation[a]
7	5	3	no abs.[b]
9	20	3	no abs.
30	4 - 8000	3 - 18	no abs.-complete S_2 abs. up to 2900 A.
700	30 - 3000	19 - 70	w. S_2 bands -s. S_2 bands
1700	30 - 3000	30 - 80	complete SO_2 abs. up to 3100 A, decreasing with increasing S_2 pressure.
10,000	30 - 3000	80 - 300	complete SO_2 abs. to 3200 A.

[a]The following abbreviations are used: abs. = absorption; w. = weak; s. = strong.

[b]Complete absorption means that the concentration of the absorbing molecule was so great that the gas was completely opaque over a wide wave-length region.

As may be seen from Table II, there was no positive evidence of the SO absorption spectrum on any of the spectrograms. E. Brackett in a similar experiment also found no trace of the SO absorption spectrum in the ultraviolet region.[18] She tried to find this spectrum by rapidly flowing SO_2 gas through a microwave discharge and sending a beam of light through the discharge products. Neither of these experiments should be taken as

evidence that the lower state of the emission system is not the ground state of SO; on the contrary the data of St. Pierre and Chipman[7a] is strong evidence that this is the case (see Appendix A). It is probable that absorption from this state does take place, but that it is masked by the diffuse spectrum of S_2 or by the strong absorption of the SO_2 molecule in the ultraviolet region. The discovery of vibrational or rotational transitions for the lower state of the electronic emission system in the infrared or microwave regions would be direct evidence that this is the ground state of the SO molecule, if the SO were produced under conditions of thermal equilibrium. In these regions the SO transitions would be unlikely to be masked by the transitions of other molecules.

Some evidence for the formation of a lower oxide of sulfur may be found in the second-to-the-last row of Table II. While this series of spectrograms was being taken the sulfur pressure was increased while the total amount of oxygen in the system remained constant. The spectrograms showed complete absorption by the SO_2 molecule up to about 3100 A. However, this absorption limit moved to lower wavelengths as the sulfur pressure was increased, indicating a slight decrease in the amount of SO_2 in the system. Rough intensity measurements were made on these uncalibrated plates at the absorption edge. According to these measurements the decrease in SO_2 absorption showed the dependence on the pressure of S_2 that one would predict by applying the law of mass action to the formation of SO gas. This decrease in SO_2 absorption was not noted under the conditions of the last row of Table II, as in this case the amount of SO formed is a smaller percentage of the SO_2 gas in the system.

APPENDIX A:

DISSOCIATION ENERGIES FOR SO AND S_2

St. Pierre and Chipman, by studying the ratios of ferrous to ferric ion in lime-iron-oxide slags in equilibrium with SO_2 gas, obtained a value for the heat of formation of SO of -18.7 ± 1 kcal per mole.[7a] Since this quantity is related to the heats of dissociation of SO, S_2, and O_2, this allows one to make a choice between the several possible values for the heats of dissociation of SO and S_2. However, in making their choice St. Pierre and Chipman used the possible values for D_0 of SO as presented by Herzberg[19] and Gaydon,[20] which are erroneous.

Herzberg apparently mistook the D_e value given on page 184 of Martin's article[3] for a D_0 value. On page 190 Martin gives the corresponding D_0 value, which disagrees considerably from that given by Herzberg. Gaydon has compounded this error by giving still another value for the higher possible D_0 value of SO, which disagrees with that of Herzberg; this is apparently a typographical error.

Let us re-examine Martin's paper to arrive at the correct possible values for D_0 of SO. He states that a breaking off of the emission spectrum due to predissociation is observed at the $K' = 6$ rotational level of the $v' = 3$ vibrational level. This leads to a predissociation limit $41,508$ cm^{-1} above the bottom of the potential curve of the lower state, or $40,948$ cm^{-1} above the $v'' = 0$ vibrational level. If we assume that the state responsible for the predissociation dissociates into normal atoms, $S(^3P) + O(^3P)$, we arrive at a D_0 for SO of $40,548 \pm 400$ cm^{-1} or 5.027 ± 0.050 ev.[*] This uncertainty arises because the molecule may dissociate into any of nine possible combinations of the triplet components of the two ^3P atoms; these possible combinations cover a range of 800.1 cm^{-1} in energy.[21] If we assume that the state dissociates into $S(^1D)$ and one of the triplet components of $O(^3P)$, then we must subtract at least 9239.0 cm^{-1} of excitation from the predissociation limit. This possibility leads to a value for D_0 of SO of $31,596 \pm 113$ cm^{-1} or 3.916 ± 0.014 ev.

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[*] A conversion factor of 8066.8 cm^{-1} per ev was used.

The resulting change in the possible values for D_0 of SO change the conclusions that one might draw about the D_0 of S_2 from the heat of formation given by St. Pierre and Chipman. Table IA is a revision of one of the tables by St. Pierre and Chipman, wherein the different possible D_0 values of SO and S_2 are combined to give all the possible values for the heat of formation of SO at $0°K$. In the revision a value for D_0 of O_2 of 117.96 ± 0.04 kcal per mole was used.[22] The possible values for D_0 of S_2 are those given by Gaydon.[20]

Table IA

Heats of formation of SO based on the possible D_0 values for SO and S_2.

D_0 of SO (kcal)	D_0 of S_2 (kcal)	$\Delta H^o_{0_f}$ for SO (kcal)
90.6	76	+ 6.4
90.6	83	+ 9.9
90.6	102	+ 19.4
115.9	76	- 18.9
115.9	83	- 15.4
115.9	102	- 5.9

We now see that the heat of formation of SO measured by St. Pierre and Chipman, $- 18.7 \pm 1$ kcal per mole, indicates that 115.9 kcal (5.027 ev) is the best value for D_0 of SO and that 76 kcal (3.3 ev) is the best value for S_2. Knudsen-cell measurements on mixtures of iron and iron sulfide by McCabe[23] also support this lower value for the heat of dissociation of S_2. Furthermore, calculations by Goldfinger and Rosen[24] based on some early vapor-pressure measurements by Wartenberg yielded a value of 3.2 ev for D_0 of S_2. Thus the values of 115.9 kcal for D_0 of SO and 76 kcal for D_0 of S_2 were used in the thermodynamic calculations in this work.

APPENDIX B:

EQUILIBRIUM CONSTANTS FOR FORMATION OF ATOMIC SULFUR

Using the value of D_0 arrived at in Appendix A, we may calculate equilibrium constants for the reaction

$$2\ S\ (gas) = S_2\ (gas). \tag{1B}$$

From a value of ΔH_0^O for reaction (1B) of -76 kcal we find ΔH_{298}^O = -77 kcal, using the heat capacities from Stull and Sinke.[15] This, in combination with the free-energy functions from Stull and Sinke, allows us to calculate equilibrium constants for Reaction (1B) at a number of temperatures as presented in Table IB.

Table IB

Calculation of equilibrium constants for Reaction (1B)
at a number of temperatures.

Temperature (^{O}K)	$(\Delta F^O - \Delta H_{298}^O)/T$ (eu)	$\Delta F^O/T$ (eu)	K
1000	27.04	50	8×10^{10}
1300	27.41	31.8	8.7×10^6
2000	28.03	10.5	2.0×10^2
3000	28.56	-2.9	2.3×10^{-1}

ACKNOWLEDGMENTS

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