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ULTRAVIOLET ABSORPTION OF SO_2: DISSOCIATION ENERGIES OF SO_2 AND SO

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ABSTRACT

The absorption intensities of SO_2 were measured in the wavelength region 2000 - 3100 Å employing the hydrogen continuum as the source and at selected wavelengths utilizing the mercury line spectrum. The pressure dependence of the absorption intensity was investigated at 1849, 2537 and 3131 Å. The existence of an absorption continuum in the spectral region 1700 - 2300 Å has been established and attributed to the dissociation of SO_2 forming SO and a ground state oxygen atom. The onset of the continuum provides an upper limit value to the dissociation energy of SO_2. The implications upon the SO_2 and SO dissociation energies are discussed.

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ULTRAVIOLET ABSORPTION OF SO_2: DISSOCIATION ENERGIES OF SO_2 AND SO

P. Warneck, F. F. Marmo and J. O. Sullivan

I. INTRODUCTION

The complex absorption spectrum of sulfur dioxide in the near and in the vacuum ultraviolet spectral region has been repeatedly studied with the aim of classifying band systems and making vibrational analyses. Specifically, in the wavelength range above 2000 Å, this has been nearly satisfactorily achieved by Duchesne and Rosen(1) and by Metropolis,(2) while the theoretical implications have been discussed by Mulliken(3) and by Walsh.(4) However, there appear to be no available data on quantitative absorption coefficients, except for the 1050 - 2100 Å spectral region, studied by Golomb et al.(5) In the present work, measurements of the SO_2 absorption intensities were obtained covering the region 2000 - 3100 Å.

An important observation in this study appears to be the finding of an absorption continuum commencing at 2280 Å. Part of this continuum can be discerned in the previously published data,(5) which also suggest the existence of a second continuum at shorter wavelengths, with the onset at 1680 Å. Since in this spectral region continua commonly arise from photodissociation processes, the observed long wavelength onset of a continuum provides an upper limit estimate for the dissociation energy of the process involved. For the two continua mentioned with onsets at 2280 and 1680 Å, the corresponding upper limits to the dissociation energies are 125 kcal and 170 kcal, respectively. It is interesting to note that the energy difference (45 kcal) between the two onsets is close to the energy required to excite the ^1D state of atomic oxygen. This factor suggests that the observed continua may be interpreted as arising from the dissociation processes:

$$(1)\quad SO_2 + h\nu \rightarrow SO + O(^3P)$$

$$(2)\quad SO_2 + h\nu \rightarrow SO + O(^1D).$$

One purpose of the present work is to show that it is reasonable to associate processes (1) and (2) to the observed continua. The importance of such data becomes evident when it is considered that the actual SO_2 dissociation energy is presently not well known and has been the subject of some controversy. Thus, after giving a description of the experiments and their results, the facts pertaining to the dissociation energies of SO_2 and the related molecules SO and S_2 will be discussed in a subsequent section.

II. EXPERIMENTAL

The principal experimental arrangement has been described.(6) In the present experiments a McPherson 2.2 m UV grating monochromator was employed in conjunction with an EMI 9514 photomultiplier detector viewing a sodium salicylate-coated glass plate. The absorption cell was 12.4 cm long, fitted with LiF windows at both ends, and mounted between detector and exit slit. In order to avoid the overlapping and interference of the first and second order spectra above 2000 Å, a quartz plate was interposed between the absorption cell and the exit slit, resulting in a short wavelength cutoff at approximately 1600 Å and a long wavelength limit around 3200 Å. The spectral range covered in the present work was from about 1850 Å to 3150 Å.

Two types of light sources were employed: (1) A windowless hydrogen discharge tube, operated at 0.5 amps and 500 volts DC, furnished the well-known hydrogen continuum which provided a suitable background for recordings of the total absorption spectrum; (2) to establish the presence of true absorption continua, additional measurements were performed at specific wavelengths utilizing the line spectrum emitted from a Hanovia Mercury Utility Lamp. In this case, the entrance section of the monochromator was sealed off by means of a quartz window. Cooling the lamp with a fan considerably improved its radiation output in the ultraviolet, making the lines at 1849, 2537 and 3131 Å sufficiently intense to study at these wavelengths the pressure dependence of the apparent absorption coefficients over a wide pressure range.

When such discrete line sources are employed the apparent absorption coefficient decreases with increasing pressure in the case of discrete absorption, whereas for a truly continuous absorption, the absorption coefficient does not vary sensitively with pressure. This behavior is due to the restricted resolution. For the case that both discrete and continuous absorption occur together, generally, the apparent absorption coefficient decreases with increasing pressure until an upper limit value for the continuum is established. Finally, for very diffuse structure the behavior is intermediate between the two cases discussed.

Matheson "bone dry" sulfur dioxide was used without further purification. A sample subjected to mass spectrometric analysis showed less than 1% impurity of either N_2 or CO, which should not alter absorption measurements in the considered spectral region. Detrimental water vapor or SO_3 was not observed. Pressures in the absorption cell were determined with a silicone oil manometer up to 25 mm Hg, while higher pressures were read on a Wallace and Tiernan No. FA129 instrument.

III. RESULTS

Intensities of absorption are shown in Figures 1 and 2 for the indicated wavelength regions. The data are expressed by the absorption coefficient k in reciprocal centimeters defined by $I = I_o \exp(-kx)$, where I_o and I are the incident and transmitted intensities and x is the layer thickness of the absorbing gas reduced to NTP. In general, absorption intensities obtained at various pressures (ranging from 2 mm Hg to 10 mm Hg) exhibited little pressure effect, so long as less than 90% of the incident radiation was absorbed in the cell. Also, under these conditions, good agreement was observed between results obtained with the mercury line source on one hand and the hydrogen lamp on the other. Consequently, most k values were derived by averaging measurements at several pressures. However, at the absorption maxima some pressure variation did occur and in this case the values given are those obtained at the lowest cell pressures. Accordingly, the presented absorption coefficients have to be regarded as apparent ones, owing to the limited spectral resolution employed.

The spectrum shown in Figures 1 and 2 suggests the presence of two continua (overlapped by bands), one between 1700 Å and 2350 Å and the other between 2400 Å and 3200 Å. However, only the first is energetically compatible with the approximately known energy value for SO_2 dissociation (vide infra) whereas the 2400 - 3200 Å apparent continuum

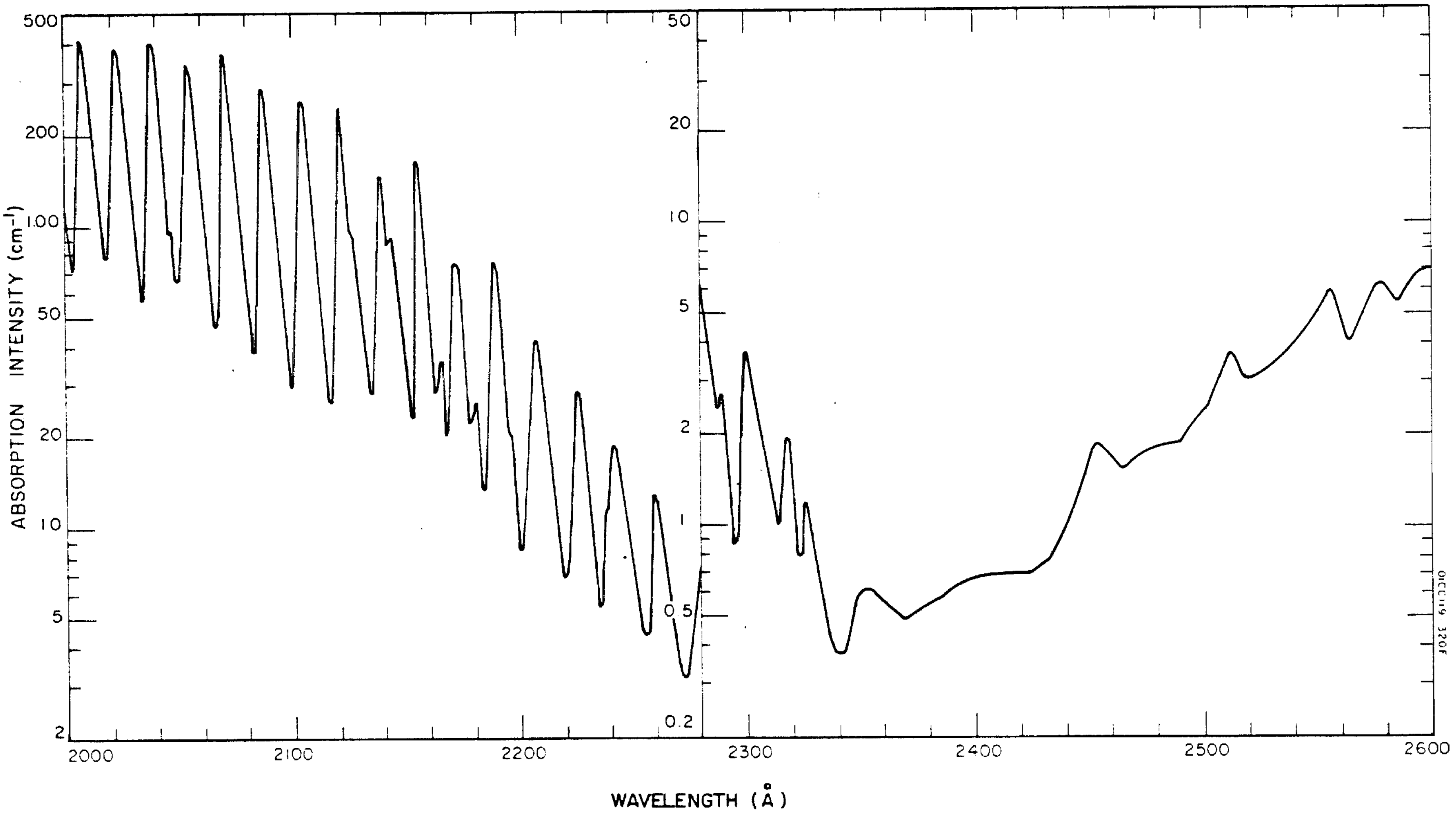

Figure 1. Absorption Intensities of SO_2 at 2000-2600 Å.

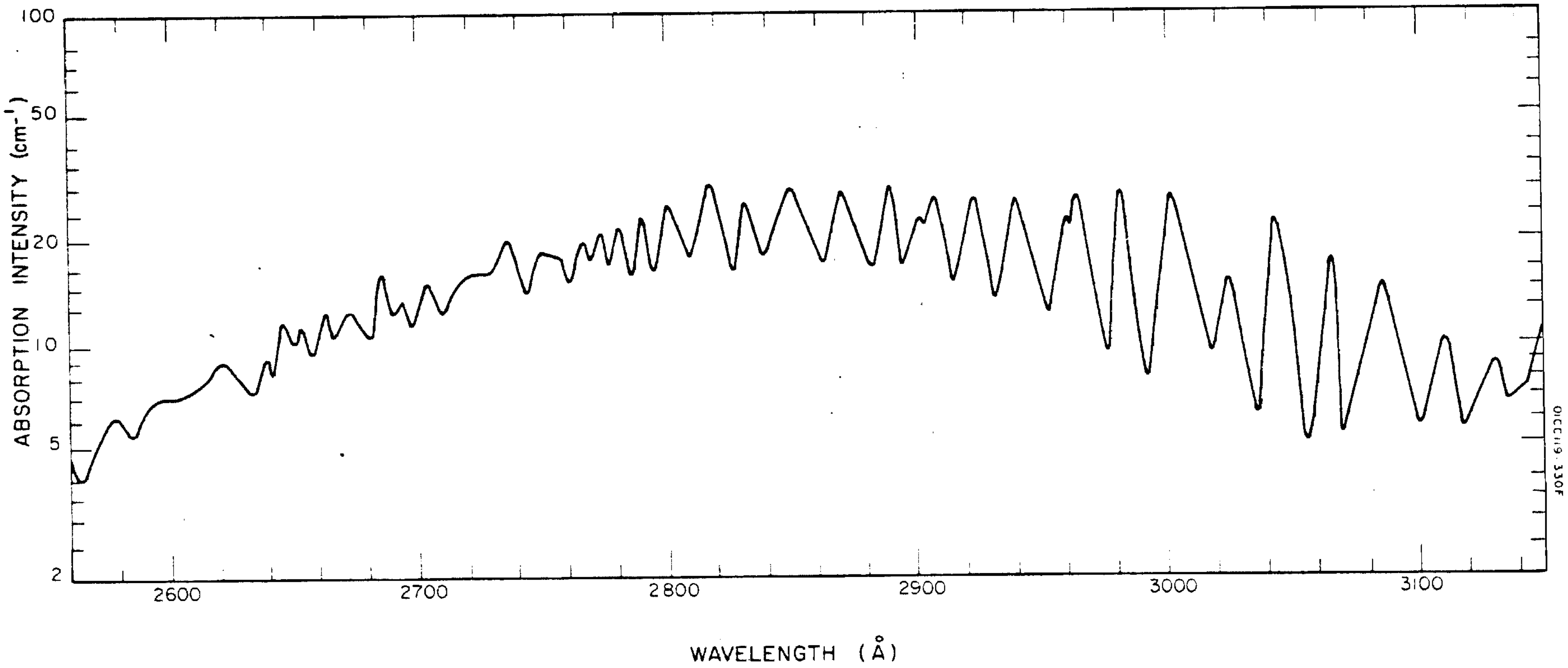

Figure 2. Absorption Intensities of SO_2 at 2560-3150 Å.

is due to the restricted spectral resolution and a considerable overlapping of the involved bands. This view is compatible with the existent spectroscopic data(7) and the present absorption experiments performed at higher pressures, with the mercury light source at the discrete wavelengths 1849 Å, 2537 Å and 3131 Å.

Characteristically, in these experiments the amount of incident radiation absorbed in the cell was more than 90%. At 1849 Å, as shown in Figure 3, the apparent absorption coefficient at first decreases with increasing pressure and then becomes essentially independent of pressure. This behavior shows the presence of a discrete absorption spectrum, but it also makes evident that in the region between 1700 Å and 2300 Å the values at the band minima can be ascribed mainly to a true continuum. It is also interesting to note that with the discrete 1849 Å source the measured absorption coefficient approaches a value for the continuum of only 28 cm^{-1} as compared to the higher value of 75 cm^{-1} previously reported.(5) This apparent discrepancy can be ascribed to the insufficient resolution obtained in the reported experiments with the hydrogen background source. Thus, it appears that a true continuum exists in the 1700 - 2300 Å region with an upper limit absorption coefficient of 28 cm^{-1} at 1849 Å.

In Figure 4 it is shown that at 2537 Å, a decrease of the apparent k-value was observed, starting at a pressure of about 150 mm Hg. However, in this case, the line intensity was insufficient to give a strong enough signal for accurate measurements above 300 mm Hg. At this pressure the

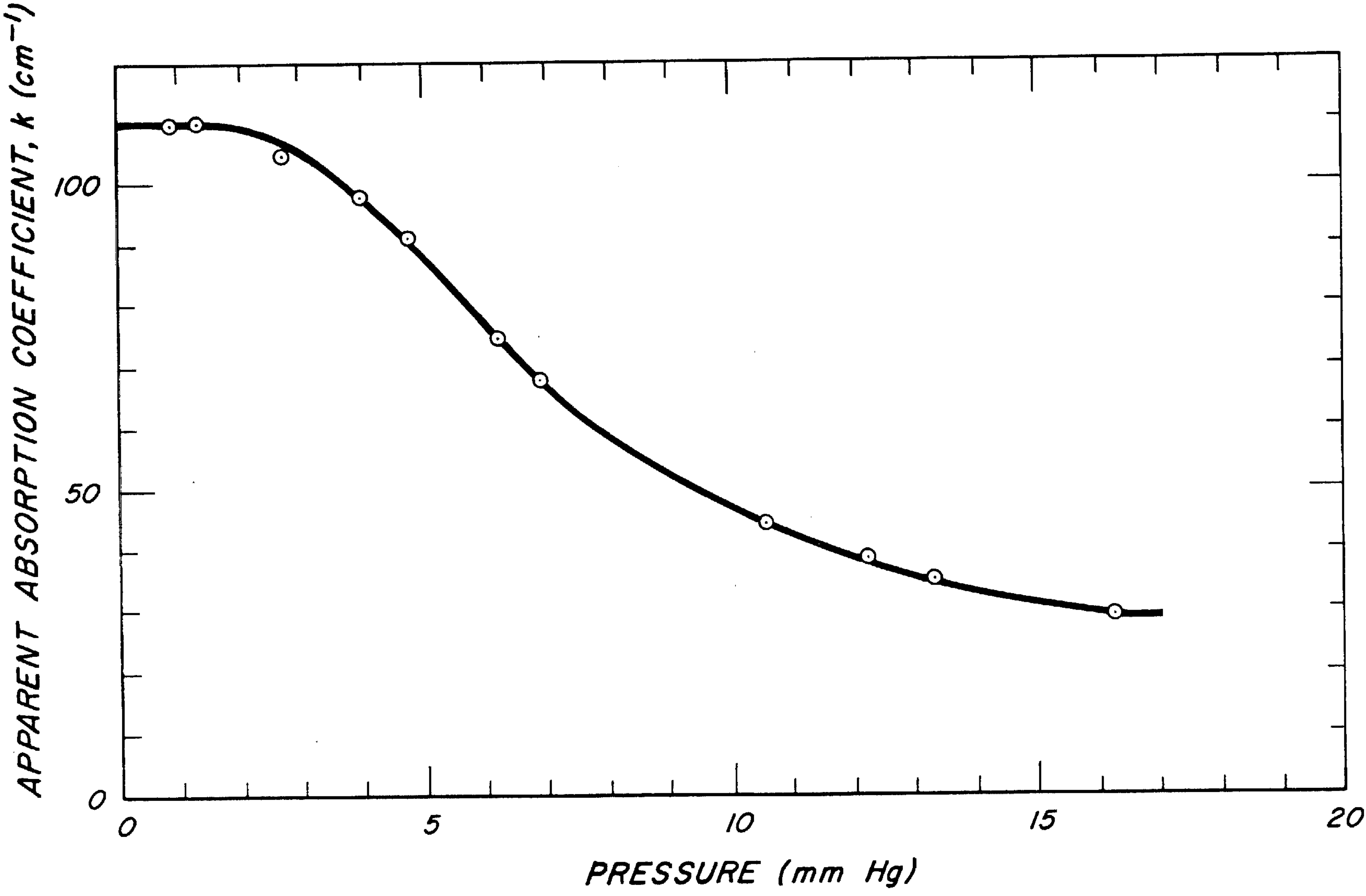

Figure 3. Pressure Variation of SO_2 Absorption at 1849 Å.

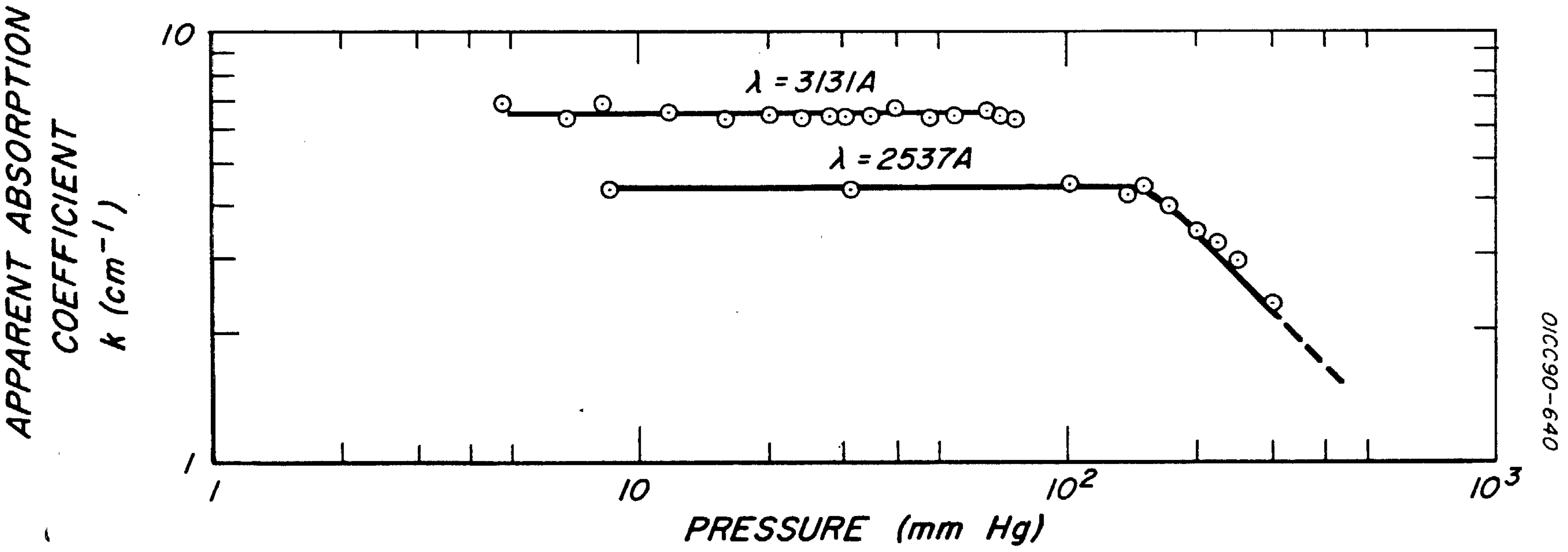

Figure 4. Pressure Variation of SO_2 Absorption at 3131 Å and 2537 Å.

apparent k-value was only 2.3 cm^{-1} (compared to 4.2 cm^{-1} at lower pressures). The apparent absorption coefficient probably decreases further with increasing pressures, suggesting that no continua exist at 2537 Å. Nevertheless, if the absorption at this wavelength should be in part continuous, the upper limit for the k-value of the continuum would be 2.3 cm^{-1}. For the 3131 Å case, no sensitive k-value decrease with pressure was observed owing to the insufficient intensity of the source. However, Figure 2 and energetic considerations preclude a continuum in this spectral region.

While the available evidence disfavors the existence of a continuum beyond 2500 Å, there can be no doubt about the reality of the observed 1700 - 2300 Å continuum. In Figure 5 are plotted the bases of the overlying bands versus wavelengths making use also of the data of Golomb *et al.*(5) The continuum is found to be quite symmetric in appearance, the maximum lying at 1915 Å and the observed long wavelength onset approximately at 2280 Å. Conventional computation gives a f-number of 0.0294, but this is probably too high because of the insufficient spectral resolution employed. If it is taken into account that with increasing pressure the 1849 Å apparent absorption coefficient decreases from $k = 75$ to $k = 28$ cm^{-1}, the corrected value is reduced to $f = 0.011$.

Also shown in Figure 5 is the continuum located below 1700 Å. Since little overlapping occurs between the two continua, the experimental long wavelength onset of the 1300 - 1700 Å continuum could be reliably

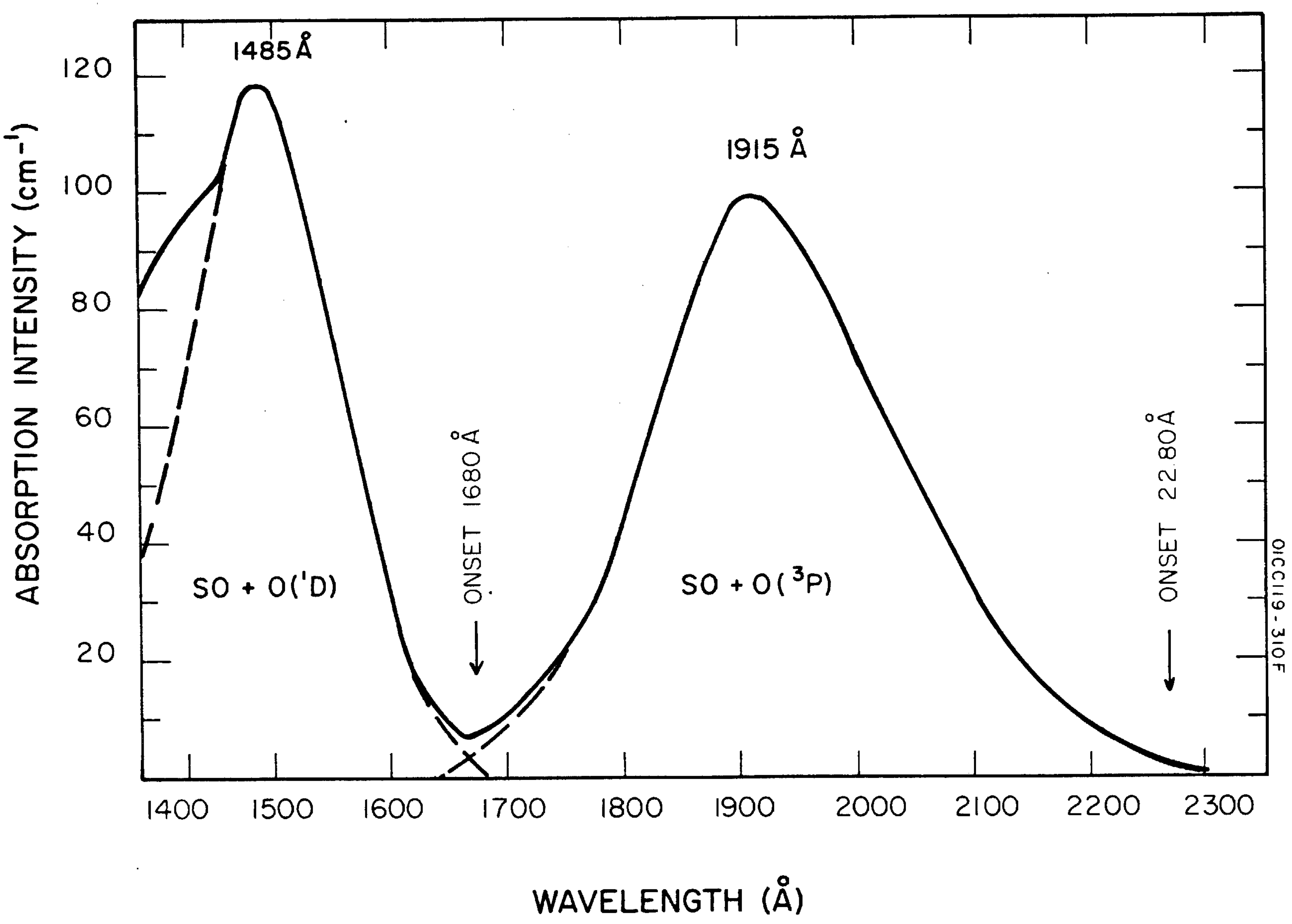

Figure 5. Absorption Continua for SO_2.

estimated to lie at 1680 Å whereas the maximum occurs at 1485 Å. The superposition of intense bands on the short wavelength slope of the continuum makes the obtained f-values somewhat ambiguous. The largest possible f-value is f = 0.0473, while the assumption of a symmetric continuum gives f = 0.035.

Undoubtedly, among the various data reported, the recognition of a true continuum in the spectral region 1700 - 2300 Å is most significant because of its implications concerning the dissociation energy of SO_2. This aspect of the results will now be discussed.

IV. THE SO_2 DISSOCIATION ENERGY

Making the reasonable assumption that at least the long wavelength end of the observed continuum is due to only one direct dissociation process, the corresponding upper limit of the dissociation energy can be determined, in principle, from the observed long wavelength onset of the continuum. Although in practice this is not a completely reliable method, in many cases it is the best available method provided the extrapolation is not too extensive.

In the present case, the long wavelength onset obtained for the two continua correspond to energies of 5.43 ev and 7.38 ev, or 125.3 kcal and 170.1 kcal, respectively. In addition, it is found that the energy difference (1.95 ev) is very close to the energy required to excite the ^1D state of atomic oxygen (1.967 ev), which makes it reasonable to associate the long wavelength parts of the two continua with the dissociation processes

$$(1) \quad SO_2 + h\nu \rightarrow SO + O(^3P); \text{ and} \qquad D\,(SO_2) \leq 125 \text{ kcal}$$

$$(2) \quad SO_2 + h\nu \rightarrow SO + O(^1D). \qquad D\,(SO_2) \leq 170 \text{ kcal}$$

with the corresponding upper limit dissociation energies as shown. Although it is difficult to give a reliable estimate of the errors involved in locating the onsets of the two continua, the derived upper limits of the dissociation energies are believed to be in error by not more than 0.2 ev, or approximately by 5 kcal.

Except for the assignment of a predissociation limit at 1950 Å by Henri(7) which has been refuted,(8) there appears to exist no direct determination of the SO_2 dissociation energy with which the present value could be compared. The energy requirement of reaction (1) can be calculated from thermochemical data by means of the relation

$$(3) \quad D(SO\text{-}O) \;=\; H(SO_6) \;+\; \frac{1}{2}\,D(S_2) \;+\; D(O_2) \;-\; D(SO)$$

provided the dissociation energies of the diatomic molecules S_2, O_2 and SO are known in addition to the heat of SO_2 formation from S_2 and O_2 in the gas phase. Unfortunately, only $D(O_2)$ = 119.1 kcal(9,10) and $H(SO_2)$ = 86.3 kcal(11) are well established, while the dissociation energies of S_2 and SO are still controversial. In both cases, fairly accurate predissociation limits are known from spectroscopic observations, but the lack of information concerning the electronic states of the product atoms precludes the proper choice among several possible values for the dissociation energies. The pertinent facts may be briefly recapitulated.

The predissociation occurring in the main SO emission spectrum is of a type for which the dissociation limit can be accurately established.(9) Martin(12) determined the limit to lie at 5.14 ev, but the SO *absorption* spectrum recorded by Norrish and Oldershaw(13) has indicated that the numbering of the vibrational levels of the ground state employed by Martin had to be revised, thus raising the predissociation limit to 5.35 ev or 123.5 kcal. If both of the atoms produced are in their ground states, this is also the dissociation energy.(14) On the other hand, if the resulting sulfur atom were in its first excited ^1D state, the dissociation energy would be lower by 1.15 ev (26.5 kcal). From a Birge-Sponer extrapolation of the vibrational levels for the upper state which is assumed to dissociate into $O(^3P)$ and $S(^1D)$, McGrath and McGarvey(15) have recently obtained D(SO) = 127.1 kcal in fair agreement with the predissociation limit of Norrish and Oldershaw.

In a similar way, an evaluation of the pertinent spectroscopic data for S_2 admits the possibilities $D(S_2)$ = 4.4, 3.6 or 3.3 ev, corresponding to 101, 83 or 76 kcal, none of which can be ruled out with certainty. The available evidence has been discussed in detail by Gaydon(14) and by Cottrell.(16)

When the various possible values for D(SO) and $D(S_2)$ are combined with the known heats of O_2 dissociation and SO_2 formation according to Equation (3), the array of SO_2 dissociation energies shown in Table 1 is obtained. Upon inspection it is found that the SO_2 dissociation energies derived with D(SO) = 97 kcal exceed by some 20 kcal the experimentally determined upper limit of $D(SO_2)$ = 125 kcal, thereby ruling out the lowest of the three possible values for D(SO). This leads at once to the acceptance of D(SO) = 123.5 kcal, or the slightly higher value of D(SO) = 127.1 kcal if the latter is shown to be more correct. Accordingly, it is also established that in the observed predissociation of SO the products are ground state atoms, i.e. $O(^3P)$, as originally suggested by Martin,(12) while the upper state $(^3\Sigma^-)$ dissociates into $O(^3P)$ and $S(^1D)$ as it was assumed by McGrath and McGarvey.(15)

TABLE 1

SO_2 DISSOCIATION ENERGIES ASSUMING VARIOUS VALUES FOR D(SO) AND $D(S_2)$

	D(OS-O)		
$D(S_2)$	D(SO) = 127.1	D(SO) = 123.5	D(SO) = 97
101	128.8	132.4	159.0
83	119.8	123.4	150.0
76	116.4	120.0	146.4

For the dissociation energy of S_2 a similar choice is not provided by the present data. This is due to the errors involved in locating the onset of the observed SO_2 dissociation continuum combined with the circumstance that only one-half of $D(S_2)$ enters into Equation (3), thus reducing the spread in $D(SO_2)$. As a consequence it is also not possible to deduce the SO_2 dissociation energy with exactitude. However, the true value for $D(SO_2)$ will lie within 6.5% of the averaged one, $D(SO_2) = 124 \pm 8$ kcal, which happens to coincide with the measured onset of the dissociation continuum.

While the preceding usage of the terms "SO_2 dissociation energy" and "$D(SO_2)$" referred to the energy required to rupture the OS-O bond as characterized by reaction (1), one must recognize the existence of the alternative mode of dissociation

$$(4) \quad SO_2 + h\nu \rightarrow S + O_2.$$

Although this process would require the breakage of two bonds, it is not permissible on this ground to exclude the reaction a priori. In the similar case of N_2O photodecomposition, it has been shown(17) that the center nitrogen atom can be ejected with some probability even though the energy is insufficient for a dissociation into three atoms. Neither can reaction (4) be excluded for energetic reasons. However, it may not be reasonable to associate the appearance of a true absorption continuum to process (4) because the breakup of the SO_2 molecule into O_2 and S must necessarily be preceded by an atomic rearrangement in the excited state, which by its nature resembles a unimolecular decomposition rather than direct dissociation along a repulsive state. The absorption spectrum would be diffuse owing to perturbations from other crossing potential curves, but would not display a true continuum. This view is still compatible with the results of the photodecomposition referenced above,(17) since in that case the interest lay in the decomposition products. The interpretation of absorption spectra on the other hand deals with the initiating step in the photodecomposition. Consequently, the given argument tends to confirm the assignment of the absorption continua to processes (1) and (2) which describe the direct dissociations.

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