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The absorption spectrum of gaseous sulphur dioxide in the ultraviolet consists of two band systems, one¹ between 3900 and 2600 Å., the other ² below 2400 Å. The second spectrum in the far ultra-violet has now been photographed down to 1600 Å. by means of a 2 metre vacuum spectrograph. An investigation of the influence of temperature on the spectrum revealed an unexpected dissociation process which forms the subject of this paper.³

The rotational structure of the SO₂ bands belonging to the second spectrum begins to disappear gradually at about 1900 Å. According to Franck, Sponer and Teller⁴ this limit of predissociation can only be interpreted as due to a dissociation of SO₂ into the unexcited products Using the value of the heat of combustion of sulphur vapour SO and O. (166 Cal.) and the spectroscopically determined data of the dissociation energy of S₂ (102.6 Cal.), O₂ (117.4 Cal.) and SO (117.6 Cal.) these authors have calculated a value of 134 Cal. as the energy necessary to dissociate SO_2 into SO and O. An appreciable photochemical decomposition of SO_2 can only be effected by light of wavelength not much differing from the limit of predissociation at 1900 Å. (150 Cal.). Results obtained by Kornfeld and Weegmann,⁵ who exposed SO₂ gas of atmospheric pressure to the light of a powerful spark, confirm this statement. They got no decomposition of SO₂ with light of λ 2537 Å., but with λ 2070 or 1860 Å. they observed a deposit of sulphur powder and the formation of SO₈ vapour. In agreement with these experiments are results obtained by Lotmar ⁶ who could excite resonance fluorescence in SO₂ vapour with light as short as 2100 Å. A noticeable optical decomposition cannot be produced with the same light which excites fluorescence.

Experimental Method.

Sulphur dioxide gas, produced from sodium bisulphate and sulphuric acid, was admitted into evacuated quartz tubes and sealed at pressures varying from 1.5 mm. to 25 mm. of mercury. The quartz tubes, 5 cm.

- ¹ Watson and Parker, *Physic. Rev.*, **37**, 1013, 1931. ² V. Henri, *Leipziger Vorträge*, p. 131, 1931.
- ⁶ A preliminary paper has been published in Nature, 130, 847, 1932.
 ⁶ Z. physik. Chem. B., 18, 88, 1932.
 ⁶ Z. Elektrochem., 36, 789, 1930.
 ⁶ Z. Physik, 83, 765, 1933.
- ⁶Z. Physik, 83, 765, 1933.

The study of the absorption spectrum of SO_2 in the Schumann region at different temperatures was carried out with the apparatus shown in Fig. 1. The absorption tube was placed in a highly evacuated silica furnace which was fixed vacuum tight between hydrogen lamp and spectrograph. The water-cooled hydrogen discharge tube was constructed after the model of Bay and Steiner.⁹ It emits a bright continuous spectrum down to about 1600 Å. when run with $o \cdot 5$ amp. Both the window of the hydrogen lamp and the window fixed between furnace and spectrograph, were of 1 mm. thick crystalline quartz and were transparent to 1450 Å. A fluorite lens, 15 cm. focus, concentrated the light on the slit. The silica furnace could be heated electrically up to 600° C. without diminishing the vacuum. But at higher temperatures the furnace gave off gas.

The photographs were taken with a 2 metre vacuum spectrograph designed by Dr. Skinner and constructed in the workshop of the Wills Physical Laboratory. The instrument is fitted with a concave speculum grating having 14,000 lines per inch, and a dispersion of 8 Å. per mm. An absorption photograph taken in the first order needs an average exposure of twenty minutes when a slit width of about 0.02 mm. and Schumann plates are used. (Oiled gelatine plates were found to be much



less sensitive in the Schumann region.) A simple mechanism enables several photographs to be taken on the same plate without breaking the vacuum. The 200 litre vessel of the spectrograph can be evacuated down to about 10^{-4} mm. mercury pressure within one hour by means of a large two-stage oil pump.

Results.

The absorption spectrum of gaseous SO_2 photographed at room temperature and at the lowest pressures used (1.5 mm. and 5 mm.) shows well-developed bands extending from 2200 to 1800 Å. with a predissociation limit at about 1900 Å. It has already been mentioned that spark light in the far ultra-violet (below 2100 Å.) is effective in producing an optical dissociation of SO_2 . Yet the light of the hydrogen lamp, even in the Schumann region, does not cause any appreciable decomposition of SO_2 . This is obviously due to the faintness of the hydrogen light, as compared with spark light. But if SO_2 is heated to 300° C., or more, the absorption spectrum changes completely. Two other band spectra appear, a very faint one of 10 bands between 2850 and 2570 Å. belonging to S_3 , and a much stronger one between 1800 and 1650 Å. which was not previously known. Parallel with the appearance of these new bands there

7 Z. Physik, 69, 728, 1931.

8 Ibid., 59, 48, 1929.

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is a fading of the SO₂ bands, as may be seen from the photometric records * reproduced in Fig. 2. The records show the absorption spectrum of SO₂, 4.5 mm. of mercury, becoming fainter with increasing temperature, and the new bands below 1800 Å. appearing at 300° C.¹⁰ The temperature effect is even more striking at lower pressures. At 1.5 mm. of mercury and 450° C. the SO₂ bands have almost completely disappeared, while the ultra-violet S₂ bands and the strong bands below 1800 Å. have about the same intensity as above at 4.5 mm. After recooling the absorption tube, the SO₂ bands reappear with the same intensity as before heating.

No trace of sulphur powder could be detected in the recooled quartz tube.



FIG. 2.—Absorption spectrum of SO₂ gas at p = 4.5 mm. and at different temperatures.

Discussion.

The presence of the ultra-violet absorption spectrum of S_2 suggests that the new bands in the Schumann region might also belong to S_2 . Attempts to express these bands in a diatomic bandhead formula proved to be unsatisfactory, although vibrational frequencies of about 722 cm.⁻¹, the ground frequency of S_2 , are present. The possibility that we might have to do with a polyatomic spectrum, due to SO_3 or to S_6 molecules, had still to be considered. This question has quite recently been definitely decided in favour of S_2 by the author in collaboration with M. Wehrli and E. Miescher,¹¹ who investigated the absorption spectrum of sulphur vapour in the Schumann region. The results confirm that the absorption power of the new S_2 bands in the Schumann region is much (perhaps ten times) stronger than that of the ultra-violet S_2 bands. Now the ultra-violet S_2 bands are much more powerful than the well-known Schumann-Runge bands (atmospheric bands) of O_2 at

⁹ I am much obliged to Dr. F. Almasy, Zurich, for his care in making these records. It was difficult to obtain smooth curves from the very unequal Schumann plates.

¹⁰ The very faint ultra-violet S_2 bands between 2850 and 2870 Å are not suitable for reproduction.

¹¹ A preliminary paper including a possible explanation of the new absorption spectrum of S_2 has appeared in *Helv. Physic. Acta*, VI, 460, 1933.

the same concentration.¹² From this it is clear that the absorption spectrum of S_2 below 1800 Å. is exceptionally suitable for observation even in minute concentrations.

The simplest explanation to account for the formation of S₂ molecules seems to be a dissociation of SO_2 into $\frac{1}{2}S_2 + O_2$, requiring 83 Cal. per mol. The spectroscopic data so far obtained would not be in contradiction with this assumption. In the experiment started with SO2 at a pressure of 1.5 mm. there must have occurred almost complete decomposition at 450° C., judged by the disappearance of the SO₂ bands. In accordance with the dissociation process given above, we expect then to find sulphur vapour of 0.75 mm. and oxygen of 1.5 mm. pressure. From the data given by Preuner and Schupp 13 we find that sulphur vapour, being a mixture of S₈, S₆, and S₂ molecules, contains about 0.5 mm. of S_2 molecules at a total pressure of 0.75 mm. and at 450° C. This is a reasonable value to account for the faint appearance of the ultra-violet S₂ bands which, according to Teves,¹⁴ can still be seen at a pressure of 0.1 mm. in a 5 cm. absorption tube. The absorption spectrum of O₂ has its maximum ¹⁵ at 1450 Å., but it does not, according to Leifson,¹⁶ reach farther than 1550 Å. at a pressure of 5 mm., in a 5 cm. tube. Thus the non-appearance of this spectrum would not be surprising in our case, where the maximal pressure of oxygen could only be 1.5 mm. Again there is no difficulty in explaining the formation of S_2 and O₂ molecules by an optical decomposition of SO₂, that is, by recombination of the photochemically produced atoms.

It is very difficult, however, to understand why a reaction requiring 83 Cal. can be influenced so greatly by raising the temperature only to 450° C. (average thermal energy = 0.7 Cal.). This somewhat startling thermal effect could perhaps be explained by a hypothesis of predissociation of polyatomic molecules as developed by Franck, Sponer and Teller.⁴ According to these authors the predissociated spectral range, which is identical with the photochemically active range, may, for polyatomic molecules, become greatly extended with increasing temperature. If that is so in our case, the continuous hydrogen light would be photochemically active over a much wider spectral range-and consequently would be much more efficient at 450° C. than at room temperature. A noticeable extension of the predissociation limit with increasing temperature cannot, however, be detected in the absorption spectrum of SO₂.

This failure suggests the adoption of the following dissociation process :---

$$SO_2 + 12.6 \text{ Cal.} = \frac{1}{6}S_2 + \frac{4}{6}SO_3.$$

The value for the reaction heat has been calculated as follows :---

 12 The intensity of the ultra-violet S_2 bands coincide with the maximum intensity of the electronic system, but the intensity of the analogous O_2 bands is much less than the maximum intensity which lies at 1450 Å.

¹³ Z. physik. Chem., 68, 129, 1910.
 ¹⁴ Dissertation, Zurich University, 1926.

¹⁵ Ladenburg, van Voorhis and Boyce, *Physic. Rev.*, **40**, 1018, 1932.
 ¹⁶ Astrophys. J., **63**, 73, 1926.
 ¹⁷ Franck, Sponer and Teller, *loc. cit.*, ⁴ p. 97.

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Assuming, as above, complete dissociation of SO₂ at a pressure of 1.5 mm. and a temperature of 450° C. we now expect to get 1.0 mm. of SO₃ and about 0.2 mm. of S₂ molecules.¹⁸ The pressure of S₂, as compared with the lowest pressure used by Teves, is still high enough to account for a faint appearance of the ultra-violet S_2 bands. Yet no trace of absorption due to SO₃ can be seen on our photographs. According to Datta¹⁹ SO₃ vapour has two continuous spectra, below 3300 Å. and below 2300 Å. respectively, the absorption coefficients of which are not known. If we keep in mind that the absorbing power of S_2 vapour (as compared with that of O_2 in the same spectral range) is extremely high, and that a continuous spectrum is less clearly visible than bandheads, it seems unlikely that the absorption spectrum of SO3 will be observable at a pressure of about I mm. The non-appearance of the SO_3 spectrum can hardly be regarded as conclusive evidence against a decomposition into S_2 and SO_3 . Two facts, on the other hand, speak in favour of this dissociation process : the low value of the reaction heat (12.6 Cal. as compared with 83 Cal.) and the results, already mentioned, of Kornfeld and Weegmann. These results can best be interpreted by an optical dissociation in the following way :---

 S_2 and SO_3 molecules will then be built up by recombination of the atoms with each other and with undissociated SO₂ molecules respectively.

It seems reasonable to assume that the same explanation holds also in our case, although our experiments have been carried out under very different conditions of pressure and light source to those of Kornfeld and Weegmann. The light of the hydrogen lamp, used in our investigation, will presumably produce a small amount of SO₃ and S₂ molecules already at room temperature, but this decomposition cannot be recognised by the spectrum of S_2 , as long as sulphur is not vaporised. The increase of the photochemical efficiency with increasing temperature -a fact which follows from the disappearance of the SO₂ bands and not from the appearance of the S_2 bands-does not seem to be incomprehensible, in case the reaction heat is only 12.6 Cal. Further experiments, which could not be undertaken during my limited stay at Bristol, are required to settle this point.

It may be mentioned here that the formation of SO_3 molecules from a mixture of SO_2 and O_2 is well known and has often been studied, especially by Bodenstein and Fink²¹ and, more recently, by Mahant.²² But their data refer to the equilibrium between SO₂, O₂ and SO₃ molecules, whereas in our case conditions are more complicated, owing to the additional presence of S_2 molecules and to the thermo-optical influence.

Summary.

The absorption spectrum of gaseous sulphur dioxide has been photographed in the Schumann region at temperatures up to 450° C. At room temperature it shows a well-developed band spectrum between 2400 and 1700 Å. with a predissociation limit at about 1900 Å., corresponding to

¹⁸ The maximum would be 0.25 mm. if no S₆ molecules were present.

 ¹⁹ Proc. Roy. Soc., 137, 366, 1932.
 ²⁰ Martin and Jenkins, Physic. Rev., 39, 549, 1932.
 ²¹ Z. physic. Chem., 60, 1, 1907.
 ²² J. Indian Chem. Soc., 9, 417, 1932.

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a dissociation into SO and O. At 450° C. and at a pressure of 1.5 mm. the bands due to SO₂ have almost completely vanished, and a new spectrum appears. This consists of very faint bands between 2800 and 2600 Å., due to S₂, and a much stronger band system below 1800 Å., which also belongs to S₂. After recooling the absorption tube, the SO₂ bands reappear with the same intensity as before heating.

As the most simple explanation a dissociation of SO₂ into $\frac{1}{2}$ S₂ and O₂ might at first sight be assumed. But this reaction requires 83 Cal. and can therefore not be so greatly influenced by temperature. A dissociation of SO₂ into $\frac{1}{6}$ S₂ and $\frac{1}{6}$ SO₃, requiring 12.6 Cal. only, is certainly more compatible with an appreciable thermal influence. The second explanation is supported also by the experiments of Kornfeld and Weegmann, who observed the formation of SO₂ and SO₃ from an optical decomposition of SO₂.

It seems reasonable, therefore, to interpret our results by a thermooptical dissociation of SO_2 into S_2 and SO_3 .

In conclusion I wish to express my sincere thanks to Professor A. M. Tyndall for having given me the opportunity of carrying out this work in the Wills Physical Laboratory at Bristol, as well as for his kind interest. I am also greatly indebted to Professor J. Franck (Göttingen) for helpful discussion.

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