THE NEAR ULTRA-VIOLET ABSORPTION BANDS
OF SO₂.

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The absorption bands of SO₂ have been measured and the number of recorded bands considerably increased. The analysis of this band system is still to a large extent arbitrary and several arrangements of the bands are possible. Since, however, the symmetric valence vibration of unexcited SO₂, as known from Raman Effect and infra-red spectrum, has nearly the same value as the vibration of the molecule SO₂, known from its band spectrum, preference is given to an arrangement of the SO₂ bands, by which the symmetric valence vibration of excited SO₂ gains almost exactly the same values as that of excited SO.

The absorption bands of sulphur dioxide in the near ultra-violet have been studied in more recent years by several authors. Dutta¹ obtained a small number of the bands whereas Watson and Parker² reported a large number of them. Dutta's analysis covers only a limited number of bands even among the bands obtained by him, whereas that of Watson and Parker is open to serious objections as pointed out by Dutta and later workers. The most serious is certainly that they obtain three different origins which is obviously impossible. Clements³ has given a new analysis of the bands recently. He has chosen a rather weak band at 31945 cm⁻¹ as the (0, 0, 0)"→(0, 0, 0)' transition on account of its behaviour under different temperatures. It should be possible indeed to single out the (0, 0, 0)"→(0, 0, 0)' band on these considerations of changes in intensity with temperature. But the particular procedure adopted by him contains a number of theoretical and experimental simplifications and therefore 31945 cm⁻¹ is not the only possible value for this transition. We have shown in this paper that the subsidiary maxima which accompany the main ones are also independent bands. Therefore intensity measurements become even more difficult because such subsidiary maxima can arise in quite different ways, e.g., by a complete overlap of a strong broad band and a weak one or by the partial overlap of two narrow bands of about equal intensity. Clements has divided the bands into two different groups—the low frequency group and the high frequency group. The high frequency group consists of composite transitions to the vibrational levels of two modes of vibrations in the excited state of the molecule from the vibrationless state of the ground level, while the low frequency group arises...
The Near Ultra-Violet Absorption Bands of \( \text{SO}_2 \)

from transitions from the vibrational levels of the excited state of the ground frequency 525 to various vibrational levels of the normal state of the molecule. This division of the bands into two distinct groups means physically that the excited vibrational levels of the ground term of the two modes 525 and 1144, which are used for the explanation of the low frequency bands, do not combine with the excited vibrational levels of the excited terms of the 1144 mode, which are used for the explanation of the high frequency bands. Theoretically a selection rule which forbids such transitions is of course not known. We have observed the bands during our study\(^4\) of the absorption of the chlorides and oxychlorides of sulphur under different conditions. We rather think it likely that all the bands are more intimately connected with one another. To our mind there are also some other reasons which go against the analysis proposed by Clements. Firstly, according to the Franck-Condon diagram, we would not expect the band at the origin to be just one of the weakest, unless of course there is an abnormal change in internuclear distances on excitation. Secondly, he obtains in the excited state of the molecule, the frequency of symmetric deforming vibration decreased while that of the symmetric valence vibration increased. On the other hand, we have found a possibility of a different analysis which has a certain advantage. It is well known from infra-red and Raman spectra\(^4\) that in \( \text{SO}_2 \) the symmetric valence vibration has about the same value as that of \( \text{SO} \) in the ground state, which again agrees with the fact that the energy of the \( \text{S}=\text{O} \) band remains very nearly constant.\(^4\) In the analysis proposed here, also the symmetric valence vibration in the excited state of \( \text{SO}_2 \) is of the same order of magnitude as that of the excited state of \( \text{SO} \). At the same time our analysis interprets the bands as a uniform system, \( i.e., \) those on the high frequency side as due to transitions from the lower vibration levels of the ground state and those on the low frequency side as transitions from higher vibrational levels of the ground state.

Experimental.

The bands were obtained in the usual way with the apparatus described elsewhere\(^4\) at different temperatures and pressures. Spectrograms were taken with pure \( \text{SO}_2 \) and with \( \text{SO}_2 \) in the presence of other vapours like \( \text{SCl}_2 \), \( \text{SOCl}_2 \), etc. The plates were run on the recording microphotometer with different enlargements. The microphotograms were then measured by an Abbe comparator, and thus the bands as well as the standard lines which were also present on the microphotogram were directly compared. Several microphotograms were measured and the wave-lengths of the bands calculated by the usual Hartmann dispersion formula agreed to 0.3 A.U. The mean value of the wave-lengths was then taken so that the accuracy obtained was within