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## VIBRATIONAL ANALYSIS OF THE 2500-3400 Å BANDS OF S<sub>2</sub>O

SCHENK and several others<sup>1-4</sup> observed an ultraviolet absorption spectrum of the products of a transformer discharge through flowing SO, and suggested SO or S<sub>2</sub>O<sub>2</sub>, as absorber of the observed spectrum. Subsequently, Meschi and investigated<sup>5.6</sup> the nature of the discharge products by mass spectrometric, stoichiometric and gas effusiometric methods and by microwave absorption spectral studies. They found from all these investigations that S<sub>2</sub>O is a major constituent of these discharge products. The microwave spectrum could be satisfactorily explained if S<sub>2</sub>O was assumed to be a bent asymmetrical molecule. Jones<sup>4</sup>, Blukis and Myers<sup>7</sup> obtained in the infrared absorption spectrum of these discharge products three peaks at 1165 cm<sup>-1</sup>, 679 cm<sup>-1</sup> and 387 cm<sup>-1</sup> which could be attributed to  $\nu_1$  the S-O stretch,  $\nu_{s}$  the S-S stretch and  $\nu_{s}$  the S-S-O bend respectively of the S<sub>2</sub>O molecule. The present studies show that the ultraviolet absorption spectrum of these discharge products is due to such an S<sub>2</sub>O molecule.

In all the earlier studies, the S<sub>2</sub>O molecules were produced in a high voltage discharge through flowing SO<sub>2</sub> and their absorption spectra studied. In our present work, they are, however, produced in an after-glow discharge in the following manner. Sulphur vapour and argon gas containing trace amounts of oxygen are passed through a side tube to which a radio frequency power of 10 MHz. 250 watts is applied. The resulting products of af discharge are pumped continuously through a 50 cm long absorption tube connected to the above side tube. Hydrogen lamp served as continuous background radiation. The absorption spectrum is recorded on a 3 m grating spectrograph having a plate factor of 5.6 A/mm.

The observed absorption spectrum extends from 2400 to 3400 Å and consists of several band progressions. Figure 1 shows a part of the absorption spectrum obtained in these studies. The bands possess in general sharp heads and only those on the short

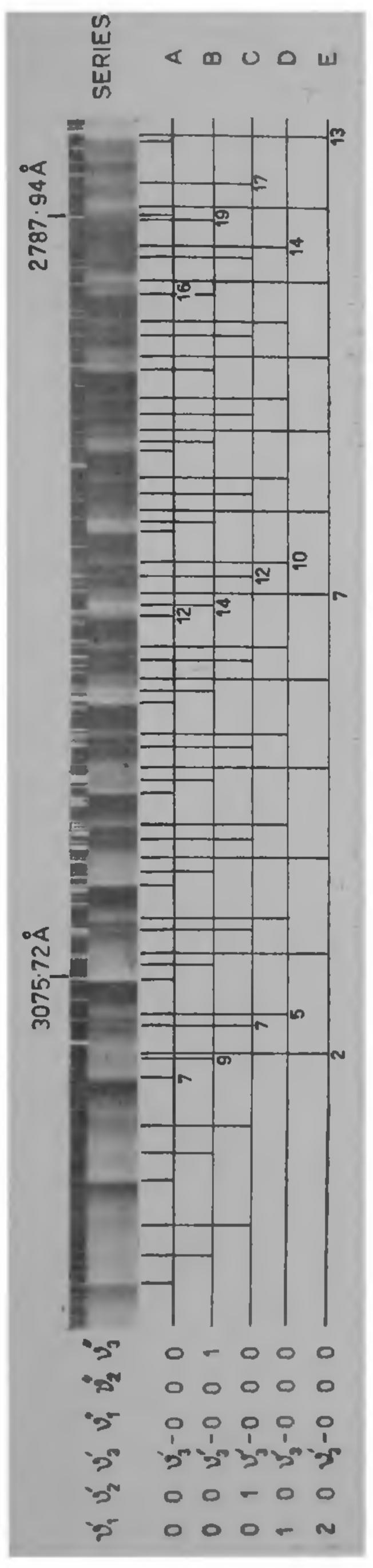


Fig. 1. Absorption spectrum of S.,O.

wavelength side become diffuse. The intensity of these bands increases towards higher members of various progressions, reaches a maximum and falls off again. The fact that the band system is extensive suggests that the S<sub>2</sub>O molecule undergoes a large change in its geometry as it goes from its ground electronic state to the excited electronic state. The 0-0 band, which was observed by Phillips et al.8 at 29285 cm<sup>-1</sup> in their matrix isolation studies of this band system, has not, however, been observed by us presumably because it is very weak. Assuming the same band origin, all the bands photographed in the present studies could be arranged into six progressions designated as A, B, C, D, E and F. Five of these arise out of 000 vibrational level of the ground electronic state to the excited electronic state involving  $v_1'$ ,  $v_2'$  and  $v_3'$  vibrational levels. The remaining one, namely, the B progression, starts from  $v_1'' = 0$ ,  $v_2'' = 0$  and  $v_3' = 1$  vibrational level and joins onto several quanta of  $v_3$  with  $v_1' = 0$ ,  $v_2' = 0$ . The progressions D, E and F involve the excitation of  $v_1$  vibrational mode with  $v_1'=1,\ 2,\ 3$  respectively over each of which are superposed the  $\psi_3$  vibrations extending to high values of  $v_3$ . The C progression, on the other hand, involves the excitation of one vibrational quantum of the bending mode  $(\nu_2)$  in the upper electronic state with the simultaneous excitation of several  $v_3$  quanta. Parts of the A, B, C, D and E progressions are indicated in Fig. 1. The bands belonging to the F progression are overlapped by other stronger bands in the spectrum shown in Fig. 1. Bands of this progression on the shorter wavelength region, however, are easily discernible. Vibrational frequencies in the ground and excited states are summarised in Table I.

Table I Vibrational frequencies of  $S_2O$  (in cm<sup>-1</sup>)

	Ground state (from infrared absorption spectrum)	Excited state (from electronic absorption spectrum)
ν <sub>1</sub> , S—O stretch	1165	1035
·	387	281
· ^ .	679	420

Details of these studies will be published elsewhere.

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## ESTIMATION OF NITROGEN IN CHROMIUM

NITROGEN in metals is usually estimated by converting it into ammonia by the Kjeldahl method1 and later determining the ammonia produced. Nessler's method is one of the simplest methods of ammonia estimation. Kruse and Mellon<sup>2</sup> have given a survey of the literature indicating the sources of interference, in the Nessler's method. Accurate estimation of nitrogen below 10 ppm is necessary when dealing with chromium where it is an embrittling impurity. Since ammonia is isolated by distillation in the Kjeldahl's method, there is no problem of interference. This communication briefly sets out the limits and precision of estimation of nitrogen in chromium metal obtainable by a combination of Kjeldahl and Nessler's method. To ensure high sensitivity reproducibility and reduce combination by extraneous ammonia, the Nessler's reagent is prepared from Analar grade chemicals and ammonia-free double distilled water. reagent is kept in dark for a week, filtered and stored in dark coloured bottles. This reagent is quite stable for a month. The ammonia-Nessler's reagent mixture requires ten minutes for full colour development for concentrations above 0.5 ppm and thirty minutes for concentrations below 0.5 ppm. Once the colour is fully developed the colour is quite stable. To counteract the absorbance due to the reagent, all absorbance values are measured with reference to a blank made with ammonia-free water in the place of the sample. Taking these precautions and measuring the absorbance at wavelength 410 nm, we find that the absorbances of 0.04 ppm and 0.4 ppm solutions are 0.0467(5 cm cell) and 0.085 (1 cm cell) respectively. The standard deviations are 0.0033 and 0.001 respectively giving a corresponding c.o.v. of 6.8 and 1.08.

In our experience we find that using a combination of Kjeldahl's and Nessler's methods, nitrogen in chromium can be estimated down to 0.5 ppm with 1 cm cell and 0.1 ppm with 5 cm cell for a 1 gm sample and 10 ml distillate.

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