

## The Far Ultraviolet Absorption Spectrum of N<sub>2</sub>O

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of that measured by us. Using the equilibrium constant as calculated above we find for 700°K, which is in our temperature range,

$$k_1/k_2 = (K_1/K_2)^2 \cdot k_1'/k_2' = 0.818 \times 2.34 = 1.92$$

according to the theory of Wheeler, Topley and Eyring. This result is based upon 14 percent additive binding in the potential surfaces, the zero-point energy of the activated state being ignored. Approximately 20 percent is required to give the experimental result for the HI reaction, if activated zero-point energy is included. However, they have used Bodenstein's experimental results to determine the proper frequencies, activation energy and moments of inertia and since the DI reaction uses the same potential surface, their result should give the correct constant for the DI reaction. Because of the difficulties involved in the theoretical calculations, however, we feel the agreement with our experimental ratio of 1.528 is highly satisfactory. Unfortunately, Wheeler, Topley and Eyring expected the observed ratios to be somewhat larger than the value cited above, since they believe their calculated frequencies for the activated complex to be too stiff. Since the experimental ratio for this reaction has been highly desirable as a check of the theory, it will no doubt suggest to the theoretical chemists the proper way to adjust the potential surfaces in

order to obtain closer agreement.

Recently, Geib and Lendle<sup>27</sup> have presented some results on the rate of formation of DI. Their ratio at 700°K is 2.45 and converting to the decomposition reaction as before by means of the equilibrium constant, we find  $k_1/k_2 = 2.00$ . This is considerably higher than our result and also somewhat higher than the theoretical one of Wheeler, Topley and Eyring. They followed the course of the reaction by measuring the extinction coefficient of iodine by a photometric method. Since they did not use monochromatic light, rather large corrections were necessary for the effect of H<sub>2</sub> and HI on the calibration curves of the iodine absorption. Their precision is therefore rather low and since their agreement with Bodenstein's results for HI is not very satisfactory, the individual rate constants, as well as their ratio, may be in error.

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He also wishes to thank Professor H. C. Urey for the donation of the deuterium oxide which was used.

<sup>27</sup> Geib and Lendle, *Zeits. f. physik. Chemie* **B32**, 463-70 (1936).

## The Far Ultraviolet Absorption Spectrum of N<sub>2</sub>O

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The absorption spectrum of nitrous oxide below 2200Å has been reinvestigated. Much new material has been found, particularly below 1550Å, including some discrete systems of bands, and some continuous regions of absorption. No bands are found below 997Å, but only continuous absorption down to about 850Å, the limit of observation. A Rydberg series was found, converging to an ionization potential of 12.66 volts. Evidence was found for a total of ten electronic states including the members of the Rydberg series. The vibration frequency in the electronic transition around 1500Å is 621 cm<sup>-1</sup>.

THE near ultraviolet absorption spectrum of N<sub>2</sub>O has been studied by many investigators.<sup>1-3</sup> The absorption above 2000Å appears

to be continuous, and very weak. Below 2000Å Leifson<sup>4</sup> found two broad bands, one whose center was apparently about 1850Å and the other extending from about 1550Å to the limit of his observation. These regions have also been studied

<sup>1</sup> A. K. Dutta, *Proc. Roy. Soc.* **A138**, 84 (1932).

<sup>2</sup> O. R. Wulf and E. H. Melvin, *Phys. Rev.* **39**, 180 (1932).

<sup>3</sup> L. Henry, *Nature* **134**, 498 (1934).

<sup>4</sup> S. Leifson, *Astrophys. J.* **63**, 73 (1926).

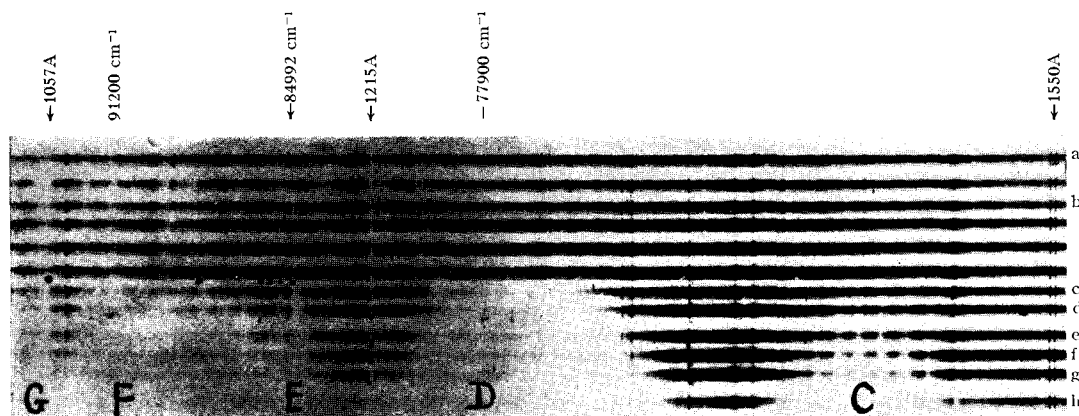


FIG. 1. (a) source, (b) N<sub>2</sub>O—0.001 mm, (c) —N<sub>2</sub>O—0.01 mm, (d) —N<sub>2</sub>O—0.02 mm, (e) N<sub>2</sub>O—0.04 mm, (f) N<sub>2</sub>O—0.075, (g) N<sub>2</sub>O—0.09 mm, (h) N<sub>2</sub>O—0.19 mm.

by Sen-Gupta<sup>5</sup> who has discussed the relation of this absorption to the decomposition of N<sub>2</sub>O into NO and N. The present writer has investigated the absorption of this molecule from 2200Å down to about 850Å and found several new regions of absorption, some of them showing vibrational structure.

#### EXPERIMENTAL

The N<sub>2</sub>O (a tank product prepared for anesthetic work) was purified by bubbling slowly through a tower filled with strong KOH solution, then dried by passing through P<sub>2</sub>O<sub>5</sub>. It was collected by liquid air in a large bulb which was attached to the spectrograph. It was then further purified by distillation with liquid air.

The spectra were photographed with a 120,000-line, 1-meter focus, glass grating used at normal incidence. The dispersion was about 8.5Å/mm in the first order. The light source was the Lyman continuum with H<sub>2</sub> used as the conducting gas in most cases. Helium, purified with charcoal and liquid air, was used in a few exposures in order to try to improve the Lyman continuum in the region 1150 to 900Å where many emission and absorption lines occur in the source. The use of helium leads to no improvement, which might have been anticipated, since most of the lines come from the glass vaporized in the discharge. In spite of this the strong bands below 1100 could be located without difficulty, but weak bands in this region may have been missed.

<sup>5</sup> P. K. Sen-Gupta, *Nature* **136**, 513 (1935).

The pressure of N<sub>2</sub>O was varied from 0.001 to 0.53 mm in this work. The spectrograph served as the absorbing column, giving a two-meter path. At these pressures no absorption whatever appeared at wave-lengths longer than 1530Å. In one exposure the spectrograph was filled to a pressure of 7.3 mm by separating the spectrograph from the discharge with a fluoride window.<sup>6</sup> The region found by Leifson and Sen-Gupta about 1850 appeared at this pressure, extending from 1768 to 2068Å. This region was not investigated further.

#### RESULTS

The general appearance of the spectrum between 1550 and 1050Å is shown in Fig. 1 which is an enlargement (about four diameters) of a representative plate.

The first electronic transition (called C) below 1550Å consists of narrow bands shaded to the red, which widen rapidly with increase in pressure. They first appear at about 0.01 mm. Above 0.1 mm the bands merge in a continuum whose limits appear to increase slowly with increasing pressure. At 0.53 mm absorption extends up to 1528Å. At 7.3 mm strong absorption extends to 1700Å, and the region between 1700 and 1768 is partly absorbed. Thus the "long wave limit" of this region given by Sen-Gupta<sup>5</sup> (1580Å) is far from constant.<sup>7</sup> The apparent

<sup>6</sup> A pressure greater than about 1 mm cannot be used in this spectrograph, because of diffusion through the slit into the discharge.

<sup>7</sup> The absorption limits in this paper are given solely for the practical use of photochemists who may wish to study the decomposition or other reactions of N<sub>2</sub>O by light in

TABLE I. Bands of electronic transition *C*.

Calc.	Obs.	Calc. - obs.
65939	65912	+27
66548	66569	-21
67135	67166	-31
67699	67697	+2
68239	68224	+15
68756	68740	+16
69251	69232	+19
69722	69745	-23
70170	70148	+22

centers of nine bands observed fit a formula

$$\nu = 65,939 + 621.2n - 11.54n^2 \quad (n=0,1,2,\dots).$$

The frequencies of these bands and the agreement with values calculated from the above equation may be seen in Table I. The bands do not appear to be very sharp but this does not imply predissociation here, since the rotational structure could not be resolved in any case with our instrument. The maximum of intensity occurs at the band 68,224  $\text{cm}^{-1}$ .

Since no discrete absorption in the ultraviolet had been reported for  $\text{N}_2\text{O}$ , we investigated the possibility that these bands might be due to  $\text{N}_2$  or to NO. We had some plates of pure  $\text{N}_2$  at pressures about 100 times that necessary to develop these  $\text{N}_2\text{O}$  bands clearly.  $\text{N}_2$  showed no absorption whatever in this region. NO present in the original gas would have been removed, but some may have been formed during exposures.<sup>2-3</sup> We then tried irradiating  $\text{N}_2\text{O}$  in the spectrograph for 30 minutes (longer than the longest exposure) with the Lyman continuum. The absorption spectrum was then taken and showed no additional bands, while the original bands were unchanged in appearance. The frequency separation is also too low for any of the known bands of NO in the Schumann region. We must conclude, therefore that these bands are due to  $\text{N}_2\text{O}$ .

these regions. It would appear that the correlation of long wave limits of continuous absorption with heats of dissociation must be carried out with great caution, for only in extremely fortunate circumstances would the relative positions of the Franck-Condon curves be such that an experimentally determined limit would have any theoretical significance. In addition, Boltzmann factors for the normal vibrations of  $\text{N}_2\text{O}$ , while small, do not exclude absorption from higher ground levels than the zero level, which further confuses the interpretation of a long wave limit. The "limit" for the next absorption region at longer wave-lengths was given as 1850Å by Sen-Gupta. Here (at 7.3 mm 200 cm column) absorption extends visibly to 2068Å.

We are unable to relate definitely the single observed excited state frequency (621) to the normal frequencies observed in the infrared. It is probably a modification of 1285.4 (N N O) or 589 (↑ N N ↓ O ↑). If the molecule remains linear in the excited state, 621 is more probably a lowering of 1285 than a modification of 589, which is not totally symmetrical. If the molecule becomes bent in the upper state no decision could be made from symmetry considerations. Resolution of the rotational structure of the bands would, of course solve the problem, since one of these frequencies is || and the other ⊥. These remarks apply also to a less complete set of bands farther in the ultraviolet where the frequency separations have comparable values.

The next electronic transition (*D*) farther in the ultraviolet shows no vibrational structure at the lowest pressures. It is first observed at a pressure of 0.002 mm, about 200  $\text{cm}^{-1}$  wide, with a center at about 77,900  $\text{cm}^{-1}$ . The region widens almost symmetrically until at 0.2 mm the limits are 82,221–73,724  $\text{cm}^{-1}$ .

At the end of this region of absorption, a region of relatively high transmission begins. At 0.05 mm it extends from 82,300 to 83,700  $\text{cm}^{-1}$ . At 0.2 mm it can still be seen though it is partly absorbed at this pressure.

Between 83,700 and about 93,000, where another transmission region begins, there are probably two electronic transitions. Corresponding to one there is a strong continuous region of absorption very similar to the transition called *D*. The center of this region is approximately 91,200 at the lowest pressure. This transition is called *F*. To the long wave-length side of this continuous region are five sharp bands which seem to be related to each other but not to the continuous absorption. There are also three other bands in this region which are more diffuse and weaker, at least in comparison with the continuous absorption. The first five bands are considered to belong to one electronic transition, called *E*. The last three bands 86,750, 87,439, and 88,241 could not be explained in any way, and may belong to still other electronic transitions. The two frequency differences between these three bands are so different that a classification with the *E* bands is not permitted. These three bands

may be seen faintly on Fig. 1, being almost lost in the continuum. The second member of the *E* bands 84,992 cm<sup>-1</sup> is the strongest of all the ultraviolet absorption bands. As will be noted in Fig. 1 this is the only band appearing on the lowest pressure spectrum (*b*). The first band, 84,397, is much weaker and we believe that it comes from the level  $v''=1$  of the normal electronic state. The difference between this and the strong band 84,992 is 595, which is equal, within our experimental error, to the fundamental perpendicular infrared frequency 589 cm<sup>-1</sup>.<sup>8</sup> The other three bands of the *E* transition are 85,473, 85,880, and 86,125. The frequency differences resemble those in the *C* transition around 1500Å, but are lower. The bands are shaded more definitely to the red than the *C* bands.

Below these bands a short transmission region (seen at the left of Fig. 1) extends to about 94,500 cm<sup>-1</sup>. There are five bands of moderate intensity at shorter wave-lengths beyond this transmission region. There is also continuous absorption all over this region. Beyond the last band measured, 100,397 cm<sup>-1</sup>, continuous absorption extends to the end of the plate, about 850Å. The centers of four of these five bands, together with the lowest pressure centers of *D* and *F* fit into a Rydberg series with the following formula:

$$\nu = 102,567 - R/(n - 0.92)^2 \quad (n = 3, 4, 5, \dots).$$

There are probably a few vibrational transitions accompanying these electronic transitions, but they are too weak to measure with certainty. These bands with values calculated from the above equation are shown in Table II. The

TABLE II. Rydberg series in N<sub>2</sub>O.

<i>n</i>	Calc.	Obs.	Calc.—obs.
3	77,202	77,900 ( <i>D</i> )	-700
4	90,999	91,200 ( <i>F</i> )	-200
5	95,975	95,852	+123
6	98,315	98,326	-11
7	99,598	99,609	-11
8	100,378	100,379	-1

<sup>8</sup> E. K. Plyler and E. F. Barker, Phys. Rev. **38**, 1827 (1931).

TABLE III. Summary of electronic states of N<sub>2</sub>O.

State	Description	Lowest pressure at which it appears (mm)
<i>B</i>	center about 1900Å, 7.3 mm	between 0.5 and 7.3
<i>C</i>	discrete bands, origin 65,939 max. intensity 68,224	0.01
<i>D</i>	continuous, center 77,900	0.002
<i>E</i>	discrete bands, origin 84,992	0.001
<i>F</i>	continuous, center 91,200	0.01
<i>G</i>	single band 94,681 Four others in Rydberg series (Table II)	0.004

ionization potential obtained by extrapolating this series, 12.66 ev, is a "vertical" (Franck-Condon) ionization potential, since the most probable transition to the upper state is measured in all cases. This is the center of absorption at the lowest pressure at which any absorption can be observed. This value may be compared with the value  $12.9 \pm 0.5$  ev obtained by electron impact<sup>9</sup> and with the vertical *I* of  $2p\pi$  of N(12.7 ev).<sup>10</sup>

Finally the electronic transitions which have been found are summarized in Table III. The band 94,681 cm<sup>-1</sup> must represent a separate electronic transition, but no explanation can be given at present of its significance. In reference to Table III, the letter *A* is reserved for the absorption above 2100Å<sup>1-3</sup> though this may prove to be a continuation of *B*.

The strongest objection to the Rydberg series above comes from the relatively low intensity of  $n=6$  as compared to  $n=5$  and  $n=7$ . This is however evident only when the three are compared at the lowest pressure. At pressures of 0.01 mm the intensities appear about the same. The strongest band in the whole spectrum does not fit into this Rydberg series. It does not fit with any other member into a series which converges to the first ionization potential. It is possible however, that it is the first member of a series converging to a higher ionization potential of this molecule, which perhaps lies at wave-length shorter than 850Å.

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<sup>9</sup> H. D. Smyth and E. C. G. Stueckelberg, Phys. Rev. **36**, 478 (1930).

<sup>10</sup> R. S. Mulliken, J. Chem. Phys. **3**, 736 (1935).