

temperature data on these two samples are given in Table I.

It is interesting to note that although the resistivity of sample *E* is about twice that of sample *F*, there is no significant difference in the temperature dependence of the resistance of the two samples. The curves for R/R_T for the two samples almost coincide and were separated by arbitrary distances in Fig. 3 for clarity in presentation. At temperatures above 20°K these curves agree remarkably with those of Tyler and Wilson⁷ on their sample *B*, where their sample *B* is most nearly like our polycrystalline graphite. These measurements, like those of Tyler and Wilson, do not seem to be simply interpreted by present theory.

In both curves in Fig. 3 the open symbols represent data taken while the sample was at a constant temperature in a liquid bath and the solid symbols represent values obtained from warmup data. While the sample was in liquid helium the temperature was controlled to 0.001°K, and in liquid nitrogen it was controlled to 0.1°K. The temperature values for the warmup points are only known to within a few degrees. However, in

Fig. 3 the warmup points from 66° to 78°K match the bath points fairly well.

In Fig. 3 the resistance is seen to rise as the temperature is lowered, as previously observed, but below 10°K it levels off. Actually, below 5°K, the resistance seems to fall very slightly. The points below 5°K have limits of error which are considerably smaller than can be seen in Fig. 3. Figure 4 shows these points on a much expanded scale. One could draw a horizontal line through these points, but curves of positive slope fit somewhat better. Even so, these curves extrapolate to absolute zero temperature almost horizontally and at resistance values slightly greater than twice the resistance at room temperature.

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Photoionization Cross Section of Nitric Oxide

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The photoionization cross section of the NO molecule was measured in the spectral region 1070–1343Å, at intervals of one to five angstroms, using a vacuum monochromator (band width 0.85Å), an absorption cell with ion collector, and a detector calibrated against a thermocouple. The ionization continuum showed some structure which was ascribed partly to preionization of several bands in the region 1070–1150Å and partly to vibrational levels of the ground state of NO⁺ ion. The photoionization cross section at Lyman alpha was 1.24×10^{-18} cm², about one-half the total absorption cross section. The first ionization potential, 9.23 ± 0.02 ev, was obtained from the long wavelength limit of the ionization continuum. Application of the method to other molecules appears promising.

INTRODUCTION

“ALTHOUGH experiments on the photoionization of air and other permanent gases have been carried out intermittently ever since the photoelectric effect was first discovered, it must be admitted that the state of our knowledge regarding the ionization of these gases is extremely unsatisfactory.” This statement made by Hughes and DuBridge¹ about twenty years ago seems to be still applicable. Experiments on photoionization have been conducted in the past mostly with vapors of the alkali metals, for their ionization potentials are low enough to permit measurements in a relatively accessible region of the spectrum between

2000 and 3200Å. In spite of the careful measurements, particularly by Mohler and co-workers (see reference 1), a review² of the data suggests that even for these atoms more consistent experimental values are desirable. Recent progress, however, has been confined almost entirely to theoretical calculations of cross sections of certain neutral and ionized atoms. The methods, results, and limitation of these calculations are discussed in papers³ by Bates and Seaton. For molecules the available information on photoionization cross sections, both experimental and theoretical, is very meager.

² T. L. Page, *Monthly Notices Roy. Astron. Soc. (London)* **99**, 385 (1939).

³ D. R. Bates, *Monthly Notices Roy. Astron. Soc. (London)* **106**, 432 (1946); D. R. Bates and M. J. Seaton, *Monthly Notices Roy. Astron. Soc. (London)* **109**, 698 (1949); M. J. Seaton, *Proc. Roy. Soc. (London)* **A208**, 408 (1951).

¹ A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932).

Very few molecules lend themselves readily to quantal methods,⁴ so that progress in this direction does not appear promising. In contrast, since it has been shown^{5,6} recently that energy measurements of dispersed radiation are not very difficult in the vacuum ultraviolet region, experimental determination of cross sections should be possible for many molecules. In fact, preliminary results for the direct photoionization of nitric oxide⁷ and molecular oxygen⁸ have already been reported.

The photoionization cross section of nitric oxide was measured in order to determine whether the formation of the *D* layer of our atmosphere might be ascribed^{9,10} to the ionization of this molecule by solar radiation in the spectral region from about 1100 to 1300Å. Absorption measurements^{7,11} in this spectral region revealed that the total absorption cross section of NO is about fifty times greater than a previous estimate,¹⁰ and since a number of diffuse bands were found overlying a region of continuous absorption, the question arose as

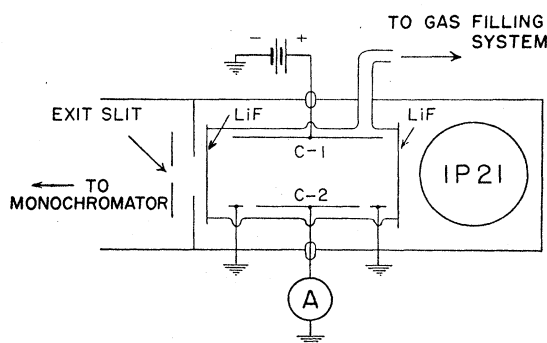


Fig. 1. Schematic diagram of photoionization cell.

to what fraction of the absorbed quanta contributed to photoionization.

EXPERIMENTAL

Most of the experimental arrangement was described in a previous paper,⁶ and here the experimental conditions will be listed. Both slits of the vacuum monochromator were fixed usually at 0.05 mm, giving a band width of 0.85Å, and this was sufficient to resolve lines about one angstrom apart. The discharge tube was operated at 0.4 amp dc with tank hydrogen flowing continuously into the monochromator where the pressure was held at about 10^{-4} mm Hg. The absorption cell was placed between the exit slit and the detector

and connected to a gas filling system provided with a pumping system, pressure gauges, and sample bottles. The total impurity of NO was less than 0.05 percent by a mass-spectrometric analysis.

The space-charge method¹² of investigating photoionization, although very sensitive to positive ions, was not used, for it does not seem to be suitable for determining cross sections. In the present work, measurements were made with a cell shown schematically in Fig. 1, which is similar to that used by Little.¹³ The cell (diameter 20 mm) and the envelope of the 1P21 tube were placed inside a vacuum tight brass box which was attached to the exit-slit mount of the monochromator. Cleaved LiF plates about 1 mm thick were used as windows of the cell. The electrodes consisted of parallel plates of platinum about 8 mm wide, placed outside of the light path. It was necessary to use rather small dimensions (lengths of C-1 and C-2 being 4.5 and 3.5 cm, respectively) so that the detector could intercept the entire beam. The two grounded electrodes served to minimize the irregularities of the electrostatic field and to confine the usable length for ion collection to C-2. The voltage required for saturation current was about 4 volts, and no difference in the ion current was found when 5 and 10 volts were applied between C-1 and C-2. The current was amplified with a Beckman micro-microammeter (RXG-2) and fed into a Speedomax recorder.

The 1P21 photomultiplier, coated with sodium salicylate was calibrated⁶ by direct comparison with a thermocouple and later checked by another observer¹⁴ in connection with the measurements of photoelectric yields of metals. Since the quantum efficiency of sodium salicylate was nearly constant⁶ in the region 850–2400Å, only a single conversion factor was used for all wavelengths between 1050 and 1350Å. Although the response of the detector was found to be linear⁶ with intensity, it was necessary to assume that the linearity held at intensities about two orders of magnitude lower than the intensities used in the calibration.

Preliminary runs with nitric oxide and other gases showed that the method was feasible. For example, photoelectric current produced by reflected and scattered light was usually negligible (less than 10^{-13} amp) compared to the ion current. For this purpose blank runs were made with the cell evacuated and with the cell filled with strongly absorbing gases such as CO₂ as well as transparent gases. After these runs, the transmittance of the right LiF window (Fig. 1) was measured and found to vary from 22 percent at 1070Å, to 56 percent (a maximum) at about 1300Å, and to 52 percent at 1380Å.

For the final runs the following procedure was used.

⁴ Buckingham, Reid, and Spence, Monthly Notices Roy. Astron. Soc. (London) **112**, 382 (1952); A. Dalgarno, Proc. Phys. Soc. (London) **A65**, 663 (1952).

⁵ D. M. Packer and C. Lock, J. Opt. Soc. Am. **41**, 699 (1951).

⁶ K. Watanabe and E. C. Y. Inn, J. Opt. Soc. Am. **43**, 32 (1953).

⁷ Watanabe, Marmo, and Inn, Phys. Rev. **90**, 155 (1953).

⁸ N. Wainfan and W. C. Walker (to be published).

⁹ M. Nicolet, Mem. Roy. Met. Inst. Belgium **19**, 1 (1945).

¹⁰ D. R. Bates and M. J. Seaton, Proc. Phys. Soc. (London) **B63**, 129 (1950).

¹¹ F. Marmo, J. Opt. Soc. Am. (to be published).

¹² Mohler, Foote, and Chenault, Phys. Rev. **27**, 37 (1926); E. O. Lawrence and N. E. Edelfson, Phys. Rev. **34**, 233 (1929); R. N. Varney and L. B. Loeb, Phys. Rev. **48**, 822 (1935).

¹³ E. M. Little, Phys. Rev. **30**, 109 (1927).

¹⁴ H. E. Hinteregger and K. Watanabe, J. Opt. Soc. Am. (to be published).

The amount of light after passing through the cell (evacuated) was measured with the detector, and the number of photons entering the cell per second was obtained by applying corrections for the absorption of the LiF window. The cell was then filled with nitric oxide at pressures from 0.49 to 10.5 mm Hg and the ion current measured as a function of wavelength by scanning the spectrum at 20Å per minute.

The total absorption cross section, σ in cm^2 , is defined by $I = I_0 \exp(-\sigma n_0 x)$, where I_0 and I are the incident and transmitted light intensities, x is the layer thickness in cm of the absorbing gas at NTP, and n_0 is the number of molecules per cm^3 at NTP. In the present case it cannot be assumed that all absorbed photons produce photoionization; some may take part in other processes such as dissociation. Hence, it is convenient to let $\sigma = \sigma_1 + \sigma_2$, where σ_1 represents the photoionization cross section and σ_2 the cross section for other processes.

To determine σ_1 from the data, the number N of photons absorbed per second in that portion of the cell length corresponding to C-2 (Fig. 1) was computed using the previously determined values of σ , and the number of ions N_1 formed per second in the same path length was obtained from the ion current. The quantity, $N_1 \sigma / N$, is then equal to σ_1 .

RESULTS AND DISCUSSION

1. Ionization Potential

Although the determination of ionization potentials and dissociation energies by electron impact is a general method, its accuracy is usually less than that of the best spectroscopic measurements. On the other hand, the latter are frequently not possible; for example, a Rydberg series may be overshadowed by other spectral lines or bands. This is the case with nitric oxide, and its first ionization potential is known only from data¹⁵ obtained by the electron impact method.

The present experiment exemplifies a third method of measuring ionization potentials: the determination of the long wavelength limit of the ionization continuum by observing the onset of ion current as the spectrum is scanned with a monochromator. This method was first carried out satisfactorily in the case of NO and was applied also to several other gases, so that the technique appears to be a general method capable of yielding accurate values of ionization potentials.

By this method the first ionization potential of NO was found to be 9.23 ± 0.02 eV, which appears to be more precise than the value 9.4 ± 0.2 eV obtained by Hagstrum.¹⁵ The long wavelength limit of ionization is shown at the extreme right in Fig. 2 by the nearly vertical portion of curve B. This limit is apparently not extremely sharp because the four indicated points spread over an interval of about five angstroms, although it is possible to resolve lines about one angstrom apart. The uncertainty of the long wavelength

¹⁵ H. D. Hagstrum, *Revs. Modern Phys.* **23**, 185 (1951).

limit and also the fact that a many-lined spectra was used as source limit the accuracy of the value given above.

The value of the first ionization potential may be helpful in the interpretation of a new emission band system recently observed by Miescher and Baer¹⁶ and by Tanaka¹⁷ but not definitely identified. The $v=0$ level of the upper state of the new band system is 73083.9 cm^{-1} above the $v=0$ level of the lower state (probably the ground state of the NO^+ ion according to Tanaka), and of the higher Rydberg series, the "γ" series,¹⁸ of NO converges at 144717 cm^{-1} . The difference of these two wave numbers is equivalent to 9.213 eV, and it is here suggested that this value also corresponds to the first ionization potential and that the new band system represents the transition from the upper ${}^1\Pi$ state to the ground ${}^1\Sigma^+$ state of the NO^+ ion as suggested by Tanaka.¹⁷ Further evidence in support of this interpretation is given in the next section.

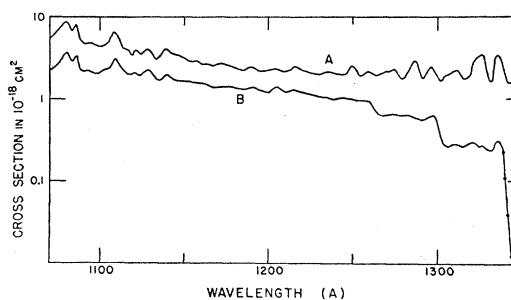


FIG. 2. Total absorption cross section (curve A) and photoionization cross section (curve B) of nitric oxide.

2. Photoionization Cross Section

In Fig. 2, curve A represents the total absorption cross section of the NO molecule in the region 1070–1350Å. This absorption curve was interpreted¹¹ as being made up of two or more overlapping continua and a number of diffuse bands. The diffuseness of these bands was indicated by the observation that the absorption cross section was very nearly independent of pressure; whereas, sharp bands showed a marked apparent pressure effect due to lack of resolution. The diffuseness may be ascribed to predissociation or preionization processes, both of which are possible in this spectral region.

The photoionization cross section of NO is shown by the lower curve, B, in Fig. 2. Both curves actually represent a series of about a hundred and fifty points and each point is a mean of several values corresponding to several pressures. A portion of the observed values of photoionization cross section is listed in Table I which shows that σ_1 is independent of pressure and nearly

¹⁶ R. Miescher and P. Baer, *Nature* **169**, 581 (1952).

¹⁷ Y. Tanaka, *J. Chem. Phys.* **21**, 562 (1953).

¹⁸ Y. Tanaka, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **39**, 456 (1942).

TABLE I. Photoionization cross sections (in 10^{-18} cm²) of nitric oxide in the region 1209–1235Å for pressures 0.49 to 10.5 mm Hg.

$\lambda(\text{Å}) \backslash P(\text{mmHg})$	0.49	0.88	1.70	4.19	10.5
1209	1.16	1.22	1.20	1.13	1.17
1211	1.14	1.22	1.20	1.13	1.19
1213	1.27	1.34	1.27	1.22	1.23
1215.5	1.37	1.16	1.21	1.22	1.25
1218.5	1.14	1.21	1.28	1.29	...
1220.5	1.11	1.22	1.17	1.25	1.17
1223.5	1.14	1.23	1.16	1.14	1.15
1226	1.23	1.19	1.06	1.04	1.02
1230	0.96	0.99	1.08	1.02	...
1234.5	1.01	1.02	1.01	0.99	1.04

constant with respect to wavelength in this region. Although the listed values are consistent, it should be noted that the absolute values may be in error by a large amount (about fifty percent) due to possible systematic errors, particularly in the detector calibration. In contrast, the estimated error for σ is only about five percent as it does not involve absolute energy measurements. From these considerations and the similarity of the two curves, particularly in the region below about 1250Å, one is tempted to suggest that curve *B* is too low by about 40 percent with respect to curve *A* and that the absorption of radiation in the region below about 1250Å by the NO molecule leads entirely to photoionization. This is admittedly a possibility. The diffuseness of the bands in the region from 1070 to 1150Å which appear in both curves is apparently due to preionization, but the σ_1 values of these bands decreased a little with increasing pressure, whereas no pressure effect was found elsewhere. Furthermore, the ratio σ_1/σ has a broad maximum at about 1200Å, so that the two curves are not entirely similar. From these data it is not possible to say that all absorption leads to photoionization.

The diffuse bands in the region above 1250Å which appear in curve *A* hardly show up in curve *B*, and any indication of these bands in the latter curve is within experimental error. Thus, the bands are apparently not preionized, and their diffuseness may be ascribed to predissociation. Moreover, the continuum underlying the bands may be partly due to a dissociation continuum which starts at about 1400Å and overlaps the ionization continuum in the region below 1343Å.

In addition to the steep rise in curve *B* at about

1343Å, there are two other places on the curve (1302Å and 1263Å) where there is an abrupt rise. The mean separation between the steps is about 2360 cm⁻¹. This is remarkably close to the differences (2339 and 2314 cm⁻¹) between the 0–0, 0–1, and 0–2 bands of the new band system^{16,17} referred to earlier. It is suggested here that the steps in curve *B* represent the ionization of NO not only to the lowest level ($v=0$) of the $1\Sigma^+$ state of the NO⁺ ion, but also to the higher vibrational levels ($v=1, 2$) of the latter state. Thus the present data including the ionization potential supports Tanaka's proposed interpretation of the new band system. Incidentally, the contributions to the ionization cross section by the vibrational levels $v=1$ and 2 appear to be greater than that by the level $v=0$, and this may be explained by the Franck-Condon principle. Furthermore, the higher value of the ionization potential obtained by the electron impact method may be explained by the fact that the latter method tends to measure the "vertical process" and not necessarily the minimum energy for ionization.

3. Applications

As mentioned earlier, the photoionization cross section of NO was measured to provide a further clue to the formation of the *D* layer. Although the data obtained here are sufficiently accurate for this purpose, uncertainties in other parameters, such as the concentration of atmospheric NO, do not warrant a detailed calculation. A note regarding the *D* layer was, however, reported.⁷

The experiments described in this paper can be applied to other molecules, and further investigations should prove fruitful. The determination of the first ionization potential of molecules by measuring the long wavelength limit of the ionization continuum might be applied as a general method. Its application to higher ionization potentials should also be possible, since in the case of the NO molecule the method was sensitive enough to bring out what appears to be vibrational levels of the ion. There are still a number of experimental difficulties; for example, it is necessary to use windowless cells in the region below 1050Å. Preliminary experiments with O₂ and other gases showed that the method is applicable even when differential pumping is used to avoid windows.