

Mass Spectrometric Study of Photoionization. VII. Nitrogen Dioxide and Nitrous Oxide*

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Photoionization efficiency curves are obtained for the molecule and fragment ions of NO_2 and N_2O from ionization threshold to 600 Å. Features of the molecule ion curves are ascribed to autoionization and the Rydberg levels are correlated with reported spectroscopic observations. The minimum onset of ionization for NO_2 occurs at 1272 Å (9.75 eV). The threshold value of 12.34 eV for the NO^+ fragment results in $D(\text{NO}-\text{O})$ of 3.09 eV in good agreement with that calculated from thermochemical heats of formation. The O^+ ion is apparently formed with 0.1 eV excess energy. The minimum threshold energy for the N_2O^+ ion is 962 Å (12.89 eV). The N_2^+ fragment ion curve has a threshold at 17.29 eV corresponding to the thermochemical bond energy, $D(\text{N}_2-\text{O}) = 1.67$ eV. However a lower-energy threshold at 15.57 eV is ascribed to ionization of molecular nitrogen from an unknown source. There is no evidence for an ion-pair process. The ground state transition for NO^+ is forbidden by spin conservation rules. The observed threshold is 0.8 eV in excess of the calculated value and suggests a vibrationally excited state of the ion. The N^+ ion is also formed with excess energy.

Key Words: Dissociation, fragment ions, ionization, mass spectrometer, molecule, NO_2 , NO_2^+ , N_2O^+ , photoionization, threshold, ultraviolet, vacuum.

1. Introduction

Studies of ionization and dissociation processes of NO_2 and N_2O are of interest both in theory and in application, particularly to the physics and chemistry of the upper atmosphere. As a result, numerous workers have reported on absorption spectra, thresholds of ionization and bond dissociation energies for both molecules.

In the case of NO_2 , Mulliken [1]¹ first postulated a molecular ionization threshold somewhat higher than that of nitric oxide and adopted [2] the value of 10 eV. No Rydberg series converging near this value has yet been detected [3, 4] for reasons now believed understood [5, 6]. However, two photoionization studies [4, 7] obtained thresholds of 9.78 eV and 9.8 eV, respectively; the former without mass analysis and the latter with mass analysis but an optical resolution of about 6 Å.

Of the many electron impact measurements reported on NO_2 in the last decade [8–12], only the ionization energies derived from fragment-ion measurements of nitroalkyls have resulted in a value near the theoretical and photoionization values 9.91 eV [11, 12]. Apparently all other measurements (including several other photoionization studies [13, 14, 15] refer to thresholds of states other than the ground state of the ion.

Recent attempts to determine the minimum ionization threshold of the N_2O^+ ion by electron impact have resulted in values ranging from 12.6 to 13.1 eV; a variation which is considerably larger than the quoted uncertainties in most of the measurements [8, 16, 17]. Unlike NO_2 , however, Rydberg absorption series converging to the first ionization threshold of N_2O have been detected and analyzed [18, 19]. In addition, photoionization measurements with [13] and without [20, 21] mass analysis indicate that the minimum ionization threshold is about 12.89 eV. Ionization thresholds for states above the ground state of the ion have been reported by electron impact, Rydberg series, and photoelectron spectroscopy [15, 22]. Of the data reported, those from the latter two sources are probably most reliable, although the first ionization threshold reported by Al-Joboury, May, and Turner [22] would appear to be too low by about 0.07 eV.

Measurements of fragment-ion thresholds have been obtained both by electron impact [8, 16] and by photoionization using mass analysis [13]. However, several inconsistencies and ambiguities appeared in the calculations of bond dissociation energies, some of which were ascribed to pyrolysis on filaments used in the electron impact studies. Of particular interest is the $D(\text{N}_2-\text{O})$ value and its relation to the exo- or endothermic nature of certain possible atmospheric reactions [23].

The purpose of the present work, part of a continuing program [24] on mass spectrometric studies of photoionization, is to obtain improved photoionization

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¹ Figures in brackets indicate the literature references at the end of this paper.

efficiency curves for the molecule and fragment ions of nitrogen dioxide and nitrous oxide and to reexamine the threshold values and the energies of dissociative ionization occurring in these molecules.

2. Experimental Procedure

The combined vacuum ultraviolet monochromator and mass spectrometer described in detail in the first paper of this series [25] was used in the present work with only the minor modifications previously reported [24]. The argon continuum was excited by a 2450 MHz, 800-W microwave discharge and used as a photon source for the NO_2^+ ion from threshold to about 1060 Å. The hydrogen many-line spectrum excited by microwave discharge or in a Hinteregger lamp was used from 1060 to 950 Å. The Hopfield continuum of helium obtained in the Hinteregger lamp was employed from 950 to 600 Å. Portions of these wavelength ranges were used for the other ions as required. Gratings, intensities of photons and ions, and probable errors were essentially as described in earlier reports. Conversion factors used are $1 \text{ eV} = 8065.73 \text{ cm}^{-1}$, and $1 \text{ eV molecule} = 23.0609 \text{ kcal mol}^{-1}$.

Both nitrogen dioxide and nitrous oxide were obtained as research grade materials from a commercial supplier. Immediately before using, they were purified of more nearly permanent gases by simple bulb to bulb distillation in a vacuum system made a part of the mass spectrometer inlet system. In addition, periodic examination of mass spectra and relative intensities of significant ions in the spectra were made during the course of all measurements to affirm the absence of changes in composition of the purified material. It is estimated from mass spectral data that impurities were less than 1 mole percent. There was no evidence for N_2O_4 in NO_2 .

Several experiments were made on NO_2 and N_2O to determine the possible occurrence of bimolecular reactions in the ion source or formation of products resulting from multiple photon impact even at the assumed low pressures existing in the ion source. All observed ion currents were simple functions of the intensity of the photon beam (at 584 Å) varied over a factor of 10 and of the sample pressure varied over a factor of 20.

As molecular nitrogen, a common residual gas in mass spectrometers, interferes with the measurements of the N_2^+ ion in N_2O , special care was taken to maintain background gases at the lowest practical value. It was frequently determined that the background ion count at $m/e = 28$ remained a small fraction < 0.1 percent of the maximum ion count for the principal ion in each gas admitted to the mass spectrometer.

3. Results and Discussion

NO_2 : The relative intensities of the NO_2^+ , NO^+ , O^+ , and N^+ ions at 584 Å (21.23 eV) are 0.49, 1.0, 0.18, and 0.003, respectively. The abundance of the

N^+ ion was too low to permit an accurate threshold determination. Also, an unsuccessful search was made for negative ions at all accessible frequencies. It is estimated that the maximum relative intensity for any ion-pair process is less than 0.01.

Figure 1 shows typical ionization efficiency curves for the NO_2^+ and NO^+ ions. The O^+ ion curve, observable only over a short wavelength range is omitted in order to simplify the figure. The abscissa is wavelength in angstroms with the equivalent energy in electron-volts given at convenient points. The ordinate is the ionization yield (ions per photon transmitted through the ionization chamber) given in arbitrary units. The ordinate scale for the NO^+ ion is one-half that of the molecule ion. The initial portion of the NO_2^+ ion curve is replotted in the inset using an ordinate scale 25 times that of the complete curve. Data points are plotted in the form of error bars; the length indicating the estimated uncertainty. Included in the figure are vertical lines of uniform length designating the location of Rydberg absorption series and progressions observed by Tanaka and Jursa [26], and the vibrational structure of a Rydberg series reported by Nakayama, Kitamura, and Watanabe [4]. In addition, vertical arrows locate ionization thresholds of nitrogen dioxide as observed by Al-Joboury and Turner [14] and Vroom [15], using photoelectron spectroscopy.

With the exception of the minimum threshold for ionization, the major features of the molecule ion curve are generally in agreement with the curves published by Weissler et al. [13], and by Frost et al. [7], although detailed comparison is not possible as those authors made observations at relatively few wavelengths and with poorer optical resolution. Our curve also shows features similar to those observed in the total ionization curve obtained by Nakayama et al., in the wavelength region 1275 to 1100 Å. The appearance of the photoionization curve in this region explains the failure of electron impact measurements and low-sensitivity techniques to observe the minimum onset of ionization.

It has been shown [5, 6] that the ground state of NO_2 is bent whereas the ion, isoelectronic with CO_2 is undoubtedly linear. Thus, the slowly rising ion yield curve appears to be characteristic of molecules undergoing structural change on ionization as noted in previous studies.

The inset of figure 1 shows the initial onset plotted on an expanded ordinate. The minimum onset definitely appears at 1272 Å ($9.75 \pm 0.01 \text{ eV}$). The uncertainty here and in following thresholds is estimated from the experimental conditions with the value of 9.78 eV selected by Nakayama et al. [4], and $9.80 \pm 0.05 \text{ eV}$ reported by Frost et al. [7]. It indicates the approximate correctness of the indirect determinations of 9.91 eV by Kandel [11] and 9.93 eV by Collin [12] although indicating that these derivations probably include some excess energy. It also supports the predicted [1, 2] low value for the ionization threshold of NO_2 and the view that all values so far obtained by Rydberg extrapolation refer to the several inner ioniza-

tion thresholds. From the absence of a strong, sharp onset, it is not surprising that spectroscopists have failed to observe the initial onset.

The initial rise of the ionization yield curve exhibits weak structure at intervals of 10 Å attributed to autoionization. Although Rydberg levels have not been reported in the wavelength region 1251 to 1144 Å, the intervals are in good agreement with the $\Delta\nu$'s observed in the 1280, 1135, and 1080 Å absorption bands and attributed to the ν_2 vibration.

The slowly rising ion yield curve in the region of 1150 to 900 Å shows partially resolved peaks attributed to autoionization. Good correlation is possible with a progression reported by Tanaka and Jursa in the 1093 to 1056 Å region, but only fragmentary evidence is obtained for the progressions reported by Nakayama et al. Furthermore, the convergence reported at 11.62 eV cannot be confirmed by our results due to the interfering autoionization peaks. The band at 940 Å has not been reported previously. It apparently converges to an onset at 915 Å (13.55 eV). Further autoionization is observed in the region of 810 to 660 Å, much of which can be correlated with the Rydberg absorption series I to IV. An additional autoionizing band is apparent below 650 Å, perhaps converging at about 20.6 eV.

Comparison of the present molecule-ion curve structure with inner ionization thresholds obtained by means of photoelectron spectroscopy is difficult because of interference from autoionization. In addition, there is a certain lack of agreement between the two sets of photoelectron data. It is apparent, however, that the latter do not include observations of the ion ground-state threshold. Also, the reported threshold at about 12.8–12.9 eV coincides with a sudden increase in a dissociative ionization process which could not be identified without mass analysis. The photoelectron threshold at 13.5 to 13.6 eV seems to be supported by a rise in the photoionization curve at that energy. Other thresholds can not be confirmed. There seems to be some inconclusive evidence from Rydberg series of ionization thresholds in NO_2 between 9.76 and ~17.5 eV. Unfortunately, only one instance of agreement is reported for photoelectron threshold with the well-established Rydberg convergence at 18.87 eV.

The photoionization yield curve for the NO^+ ion (fig. 1) shows a very weak onset at 1005 Å (12.34 eV) and includes evidence for autoionization. It is followed by a much more intense onset at 953 Å (13.01 eV). The latter increase coincides with a peak in the molecule ion curve attributed to an autoionizing Rydberg level. It is suggested that this level may autoionize either to the parent ion or to a fragment ion. Similar instances of competing processes have been observed in previous studies and the conclusion is further supported by the intense autoionization observed in the region 810 to 600 Å, some of which can be correlated directly with similar peaks in the molecule ion curve.

The threshold value of 12.34 eV, less 9.25 eV for the ionization energy of NO [21], gives 3.09 eV

for the heat of reaction at 0 °K for the process, $\text{NO}_2 \rightarrow \text{NO} + \text{O}$. We find this in very satisfactory agreement with the value of 3.115 eV calculated from the appropriate heats of formation [27] at 0 °K. There is no evidence for a lower-energy threshold such as would correspond to an ion-pair process, $\text{NO}_2 + h\nu \rightarrow \text{NO}^+ + \text{O}^-$.

The shape of the ionization efficiency curve (not shown) for the O^+ ion from $\text{NO}_2 + h\nu \rightarrow \text{O}^+ + \text{NO}$ is quite similar to the NO^+ curve. A very weak and slowly rising onset appears at 737 Å (16.82 eV) followed by a much sharper and more intense onset at 657 Å (18.87 eV). Subtracting the ionization energy of atomic oxygen [28] from the minimum threshold gives 3.22 eV for the heat of reaction compared with the above calculated value of 3.115 eV. Apparently about 0.1 eV of excess energy is included in this reaction. Transition to the ground state is forbidden by spin-conservation rules.

N_2O : Relative intensities of the N_2O^+ , NO^+ , N_2^+ , O^+ , and N^+ ions were found to be 1.00, 0.59, 0.16, 0.02, and 0.03, respectively, at 584 Å (21.33 eV). Relative intensities of the fragment ions measured at 600 Å by Weissler et al. [13], are much larger and suggest the possibility of impurities due to inadequate pumping facilities.

An O^- ion was observed with a maximum intensity at about 800 Å. Unfortunately, the abundance (estimated to be about 0.001 relative to the molecule ion abundance) is too weak to permit satisfactory measurements of the ionization efficiency curve. Curves were obtained for all the observed positive ions although only the molecule and the N_2^+ ions are shown in figure 2, and the NO^+ ion curve is shown in figure 3. The remaining curves are omitted in order to simplify the figures. Various progressions and Rydberg series observed by Tanaka et al. [19], and the onsets of ionization by means of photoelectron spectroscopy reported by Al-Joboury et al. [22], and by Vroom [15] are indicated in figure 2 in the same manner as in figure 1.

The minimum threshold of ionization for the N_2O^+ ion appears to be a sharp, intense onset with a total energy spread of about 2 Å. As this is essentially the band width of the photon beam, we take the midpoint, 962 Å (12.887 ± 0.007 eV) to be the value of the initial ionization energy. This is in excellent agreement with the value of 12.889 eV obtained by extrapolation of Rydberg absorption series [19] and of 12.882 ± 0.008 eV [21] and 12.90 ± 0.01 eV [20] obtained by photoionization without mass analysis. These concordant results apparently rule out the lower value of 12.712 eV obtained by Duncan [18]. The two values obtained by photoelectron spectroscopy, 12.82 eV [22] and 12.90 ± 0.01 eV [15] are not consistent within the uncertainties suggested by the number of significant figures, although our measurements agree with the second value. We are not in agreement with recent electron impact values of 13.09 ± 0.05 eV [8] and 12.63 ± 0.05 eV [16].

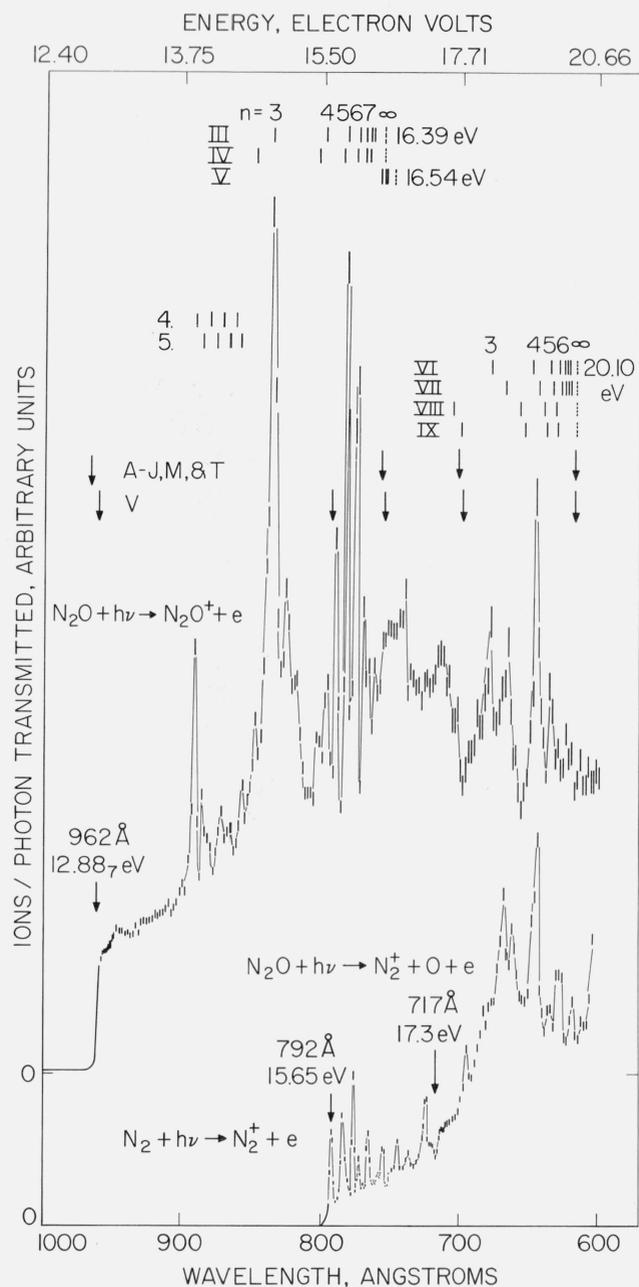


FIGURE 2. Photoionization yield curves for the N_2O^+ and N_2^+ ions of N_2O .

Tanaka et al. [19], observed two Rydberg series of absorption bands converging to 104,000 and 104,300 cm^{-1} , respectively, which they ascribed to the two components of the $^2\Pi$ ground state of the N_2O^+ ion. Although their $\Delta\nu = 300\text{ cm}^{-1}$ is in poor agreement with the value of 133.1 cm^{-1} obtained by Callomon [29] for the splitting of the $^2\Pi$ state, the discrepancy is ascribed [30] to the fact that the second Rydberg series could not be followed to very high members. It is not possible to resolve this matter in the present work, although there is evidence for two additional

onsets at about 950 and 935 Å. These may represent doubly excited bending frequencies or totally symmetric stretching frequencies. However, no previous observations of Rydberg series leading to vibrationally excited ground states of the ion have been reported.

Below 900 Å, partially resolved peaks ascribed to autoionization are observed at wavelengths that are in excellent agreement with those of the weak, diffuse progressions numbered 4 and 5 by Tanaka et al. This is followed by two groups of intense autoionization peaks in the region 850 to 770 Å which are easily correlated with the Rydberg absorption series III, IV, and V converging to the limits of 16.39 eV and 16.54 eV. These limits are not apparent in the present work but the first of these is in good agreement with a threshold of ionization observed by photoelectron spectroscopy [15, 22].

Other autoionization peaks are observed in the region 700 to 630 Å. These are also correlated with the Rydberg absorption series VI and VII. It is interesting to note that there is also evidence for minima in the photoionization curve in this region that apparently correspond to Rydberg levels in the emission series VIII and IX as reported by Tanaka. Again, there is no appearance of an onset [31] at the convergence limit of 20.10 eV although it is apparently confirmed by photoelectron spectroscopy [15, 22].

The photoionization efficiency curve for the N_2^+ ion shown in figure 2 is of particular interest. The midpoint of a sharply rising onset first appears at 796 Å (15.576 eV) with a peak maximum at 792 Å (15.65 eV). The full-width at half maximum is approximately equal to the optical resolution. Other peaks follow at about 10 Å intervals to 720 Å. A sharp increase in continuum occurs at 717 Å (17.29 eV) and again at 700 Å (17.71 eV) followed by considerable autoionization in the region 670 to 600 Å. Assuming the onset at 17.29 eV to represent the threshold for the dissociative ionization process, $N_2O + h\nu \rightarrow N_2^+ + O + e$, subtracting the ionization energy, $I(N_2) = 15.576\text{ eV}$ [32] gives the bond dissociation energy, $D(N_2 - O) = 1.71\text{ eV}$. Within the obvious uncertainty of evaluating and interpreting the threshold, this value is in agreement with $D(N_2 - O) = 1.671\text{ eV}$ calculated from thermochemical heats of formation [27] at 0 °K.

Unfortunately, the interpretation of the low energy threshold and the origin of the autoionization peaks in the wavelength region 792 to 722 Å is somewhat ambiguous. One possible interpretation is the dissociative ionization of Rydberg levels in the N_2O molecule (predissociation) to yield ion-pairs according to the process, $N_2O + h\nu \rightarrow [N_2O^*] \rightarrow N_2^+ + O^-$. In which case the minimum threshold will appear at an energy lower than the ion-neutral process by an amount equal to the electron affinity of the oxygen atom, $EA(O) = 1.48\text{ eV}$ [33] or at 15.81 eV (784 Å). The discrepancy in the observed value is -0.16 eV .

Curran and Fox [16] reported an analogous observation in an electron-impact study of N_2O . They observed an onset of ionization below that of the ion-neutral process but ascribed it to the ionization of molecular nitrogen formed by the pyrolysis of

N₂O in their heated ion source. Pyrolysis is ruled out in the present experiments as the ion source operates at ambient room temperature. Formation by multiple photon collision or by means of a bimolecular reaction is also excluded as indicated in the section on experimental procedure. Thus the possibility remains that the threshold for the ion-neutral process includes excess energy and that the N₂-O bond dissociation energy (1.671 eV) calculated from heats of formation is too high by at least 0.16 eV. There is some evidence in support of this suggestion [16, 23, 34].

In the present measurements, however, it is possible to compare the wavelengths of the autoionizing Rydberg levels for the several molecular species involved. For example, if the N₂⁺ ion is due to ion-pair formation by dissociative autoionization of Rydberg levels in the N₂O molecule, then peaks in the molecule ion curve, reflected in the ion pair curves, should appear at the same wavelength in the latter (N₂⁺, O⁻) curves. Table 1 lists wavelengths and estimated relative intensities for principal peaks observed in the wavelength region 790 to 690 Å of the N₂⁺ and N₂O⁺ ion curves of figure 2. It also includes the wavelengths and ionization coefficient (*k_i*) values of the maxima previously observed in total photoionization curves of N₂O [35] and N₂ [36].

TABLE 1. Comparison of maxima observed in the 792-694 Å region of the ionization efficiency curves of N₂O and N₂

Mass analysis				Total ionization			
N ₂ ⁺		N ₂ O ⁺		N ₂ O ^a		N ₂ ^b	
λ	I ^c	λ	I ^c	λ	<i>k_i</i> (cm ⁻¹)	λ	<i>k_i</i> (cm ⁻¹)
792	0.6	790	.7	789.5	810	792.0	1000
784	.7	782	1.0	782.5	1000	783.5	1040
776	1.0	774	0.9	774.0	850	776.0	1060
772	0.4	770	.6	769.5	600	771.5	750
765	.6	767	.5	767.0	540	765.0	940
758	.4	762	.5	762.5	485	758.5	600
754	.5	750	.6	750.0	500	754.3	940
744	.5	740	.6	740.0	540	743.7	680
736	.4	730	.5	730.0	530	736.8	570
723	.8					723.4	1100
694	.4					694.9	800

^a Reference [35].

^b Reference [36].

^c Relative intensities estimated from peak heights.

^d Corrected for estimated N₂⁺ from ion-neutral process.

Although the relative intensities of the maxima observed in the present work are of qualitative significance only, it is clear that the wavelength positions for the maxima in the N₂⁺ ion (fig. 2) in the region 792 to 694 Å correspond within 0.5 Å to maxima in the absorption curve of molecular nitrogen and that they differ by 2 Å or more from the maxima observed in the molecule-ion curve. Furthermore, we have obtained the photoionization curve for the molecule ion of nitrogen and, in the wavelength region 792 to 694 Å, we find the onset and maxima to be identical with that region of the N₂⁺ curve in figure 2 whereas the peaks at shorter wavelengths are due to N₂O, only. We must conclude, that the low-energy process observed here is due principally to the photoionization of molecular

nitrogen. The ion-pair process may occur with low probability but it is obscured by the ionization of nitrogen.

The ionization coefficients for N₂O and N₂ in the above wavelength region have been tabulated [35, 36]. For example, at 733 ± 1 Å the minimum *k_i* values for N₂O and N₂ are approximately equal (500 cm⁻¹). From that fact and the observed intensity of the N₂⁺ ion, we estimate the presence of about 3 mole percent nitrogen in the ion source. As this is an order of magnitude greater than anticipated from the purified sample or measured as background (without introduction of sample), the origin is presently unexplained.

The ionization efficiency curve of the NO⁺ ion from N₂O is plotted in figure 3 in the same manner as figure 2. A sharp but relatively weak onset at 828 Å (15.01 eV) is followed by autoionization peaks at intervals of about 8 Å in the region 820 to 770 Å. These are ascribed to Rydberg levels apparently converging to a second, more intense onset at 750 Å (16.53 eV). The associated continuum shows some evidence of autoionization and a third onset at 699 Å (17.74 eV).

The threshold at 15.01 eV, ascribed to the process N₂O + *hν* → NO⁺(X'Σ⁺) + N(⁴S^o), is in good agreement with the less precise electron impact value of 15 eV [8] but considerably higher than the more recent value of 13.75 ± 0.01 eV [16]. Subtracting the ionization energy, I(NO) = 9.250 eV [21] from 15.01 eV gives D(N-NO) = 5.76 eV (132.4 kcal mol⁻¹). The appropriate heats of formation [27] at 0 °K result in a value of 4.924 eV (113.55 kcal mol⁻¹). Thus the observed threshold includes 0.84 eV excess energy and this is consistent with the expectation that a transition to the ground state of the products from N₂O(X'Σ⁺) is forbidden by spin conservation rules. The excess energy probably appears as a vibrationally excited ion as Nicholson [21] reports the 0-3 vibrational interval of the NO⁺(X'Σ⁺) to be 0.855 eV.

The second and third thresholds at 16.53 and 17.74 eV are ascribed to the formation of NO⁺ in the ground state and N atoms in the ²D^o and ²P^o states, respectively. The observed threshold of 16.53 eV for the reaction N₂O(X'Σ⁺) + *hν* → NO⁺(XΣ⁺) + N(²D^o) + *e* is in excellent agreement with the calculated value of 16.557 eV using heats of formation of the ground state species and the (⁴S^o - ²D^o) interval of 2.383 eV [28]. Similarly, the observed threshold at 17.74 eV for the reaction, N₂O(X'Σ⁺) + *hν* → NO⁺(X'Σ⁺) + N(²P^o) + *e* is in good agreement with 17.749 eV calculated by means of the (⁴S^o - ²P^o) interval of 3.575 eV [28].

The O⁺ ion curve (not shown) has a weak onset at 810 Å (15.31 eV) followed by considerable autoionization in the range 800 to 740 Å. The well-defined peaks appeared at about 7-Å intervals and at wavelengths identical with peaks observed in the molecule ion curve (see fig. 2). The threshold at 15.31 eV is in good agreement with electron impact values of 15.33 ± 0.02 eV [8], and 15.49 ± 0.10 eV [16] and with the threshold of 15.289 eV at 0 °K calculated from heats of formation for the reaction, N₂O + *hν* → O⁺ + N₂ + *e*.

The N⁺ ion is measurable only over a relatively short wavelength region. However, a very sharp onset

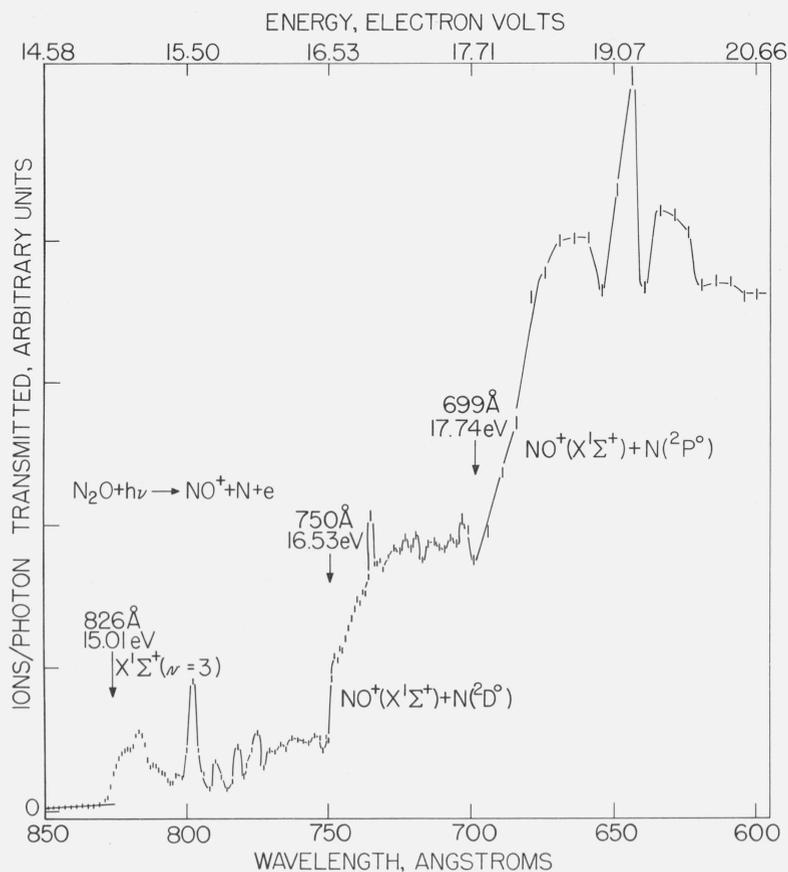


FIGURE 3. Photoionization yield curve for the NO^+ ion of N_2O .

is observed at 618 Å (20.06 eV) followed by a fairly smooth increase in continuum to 600 Å. The heats of formation result in a calculated threshold of 19.456 eV at 0 °K for the reaction, $\text{N}_2\text{O} + h\nu \rightarrow \text{N}^+ + \text{NO} + e$. Thus about 0.6 eV excess energy is included in the dissociative ionization process.

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