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DISSOCIATIVE AND DOUBLE PHOTOIONIZATION CROSS SECTIONS
OF NO FROM THRESHOLD TO 120 Å

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ABSTRACT

The partial photoionization cross sections for producing the NO⁺ parent ion and the O⁺, N⁺, and NO²⁺ fragment ions from neutral NO are presented from 120 to 614 Å. The results indicate predissociation of the c ³Π (21.72 eV) and B' ¹Σ⁺ (22.73 eV) electronic states of NO⁺. The photoionization threshold for double ionization was found to be 39.4 ± 0.12 eV.

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INTRODUCTION

The absorption structure and total absorption cross sections of nitric oxide have been studied extensively, particularly, from about 2000 to 600 Å.¹⁻⁵ Continuum cross section measurements were extended to shorter wavelengths by use of synchrotron radiation^{6,7} and a continuum spark discharge light source.⁸ However, although a few measurements have been made of dissociative photoionization of NO there are no detailed studies. The earliest measurements, made in 1958 by Weissler et al.⁹ at a few discrete wavelengths, revealed O⁺ and N⁺ fragments near their respective ionization thresholds. More recently, the same region was studied by Hertz et al.¹⁰ using synchrotron radiation, which revealed interesting autoionization structure superimposed on the O⁺ yield curve. Kronebusch and Berkowitz¹¹ measured the ratio of the O⁺ and N⁺ fragments with respect to NO⁺ at a few wavelengths between 304 and 584 Å. However, all of the above measurements were on a relative basis and none took into account the discrimination effect caused by energetic fragment ions. The present work presents absolute dissociative photoionization cross sections for the production of NO⁺, N⁺, O⁺, and NO²⁺ fragments from NO over the wavelength range from 120 to 614 Å. Unpublished data have also been obtained by Brion and co-workers¹² by use of the dipole (e, e + ion) scattering technique that simulates photoionization mass spectrometry.¹³

EXPERIMENTAL

A time-of-flight (TOF) and a conventional magnetic sector mass spectrometer were used to study the ions produced by dissociative photoionization.¹⁴ The ionizing radiation sources used were (a) a dc glow discharge in helium to produce the HeI 584 Å and HeII 304 Å lines, (b) a high voltage condensed spark discharge in Ar to produce numerous discrete emission lines between 100 and 1000 Å, and (c) synchrotron radiation from the storage ring at the Physical Sciences Laboratory of the University of Wisconsin. The synchrotron radiation was used with the TOF mass spectrometer in conjunction with a normal incidence monochromator, which covered the spectral range from 300 to 700 Å. The spark source was used with the magnetic sector mass spectrometer and a grazing incidence monochromator from 120 to 440 Å.

The TOF mass spectrometer was designed to observe energetic fragment ions in the range 0 to 20 eV with little or no discrimination.¹⁴ This was achieved by providing a sufficiently high extraction field in the ionization region of the mass spectrometer and using a large 40 mm diameter channel electron multiplier array to detect the ions.

The data obtained from the time-of-flight mass spectrometer were analyzed by the branching ratio method. That is, the cross section σ_j , for a specific dissociative ionization process that produces the fragmentation j is given by

$$\sigma_j(\lambda) = [N_j(\lambda)/\Sigma N_j(\lambda)]\sigma_t(\lambda) , \quad (1)$$

where the term in the square brackets is the branching ratio, $N_j(\lambda)$ is the number of ions of type j , and $\sigma_t(\lambda)$ is the total photoionization cross section. This method provides accurate partial cross sections provided no ions are lost or discriminated against because of varying ion kinetic energies.

The magnetic sector mass spectrometer, like all instruments of this type (narrow entrance and exit slits), does discriminate against ions of different kinetic energy. Never-the-less it can be extremely useful when operated in the ions/photon mode, as discussed below. Also, because of its very efficient ion collecting optics it could readily be used with conventional pico-ammeters. This allowed use of our intense laboratory spark light source with its wide spectral range. The spark source emits micro-second pulses and, therefore, is not readily adapted to digital counting methods.

To avoid the major problem of ion discrimination with this mass spectrometer we did not measure the ratios of different ions. Instead the ratio of the number of ions of a given type to the intensity of the ionizing radiation was measured as a function of wavelength. With the low pressure used in the ion chamber this ratio of ions/photon is directly proportional to the photoionization cross section for this process. These relative cross sections were then placed on an absolute basis by normalizing them to the data obtained at 304 Å with the TOF mass spectrometer. The intensity of the incident radiation was measured with a calibrated electron multiplier.

This method can be expected to give good results when the kinetic energy of the ions remains constant as a function of wavelength (this is certainly true for the parent NO^+ and NO_2^+ ions) or when the ion energies are very low, as frequently encountered near the lowest threshold for dissociative photoionization.

The sample gas, supplied by the Matheson Co., was used without further purification. The gas pressure was kept constant at about 7×10^{-5} Torr with a pressure controller. The background pressure was about 1.5×10^{-6} Torr when a liquid nitrogen trap was used on top of the ionization region. The bandpass of the normal incidence monochromator was about 3.3 \AA (FWHM), and about 1 \AA for the grazing incidence monochromator.

RESULTS AND DISCUSSION

Absolute branching ratios for NO^+ , O^+ , and N^+ ions were measured with the TOF mass spectrometer from 304 to 614 \AA . The absolute dissociative photoionization cross sections for producing these ions were obtained by multiplying the branching ratios with the total photoionization cross sections of NO as obtained by Brion *et al.*¹² To extend the data to shorter wavelengths relative photoionization cross sections were measured by use of the magnetic sector mass spectrometer down to 120 \AA . The relative data were then normalized to the absolute data at 304 \AA .

Because the NO^+ ions are all formed with constant thermal energy the ratio of ions/photon provides a true relative cross section for NO^+ at all wavelengths. Measurements were made between 120 and 490 \AA . This provided an overlap of the two sets of data between 304 and 490 \AA . The majority of the two sets of data points coincided within a few percent of each other,

as can be seen in Fig. 1. Thus, absolute NO^+ cross sections were obtained over the entire spectral range from 120 to 614 \AA . The smooth line drawn through the data points represents the best fit to the data and these results are tabulated in Table I. When these results are subtracted from the total photoionization cross sections we obtain the cross section, $\sigma(\text{fragments})$, for producing fragment ions of all types, excluding NO^+ . These results are also shown in Fig. 1 by the smooth continuous line and are tabulated in Table I.

The NO^{2+} ions were also formed with constant thermal energy and, therefore, the ratio of ions/photon represents the true relative cross section for producing the doubly ionized ions. These ions were measured with the magnetic mass spectrometer only. The relative data were put on an absolute basis by normalizing them, to provide a best fit between 210 and 260 \AA , with the absolute NO^{2+} cross sections obtained by Brion *et al.*¹² The results are shown in Fig. 2 and agree well with the shape of Brion's curve except at the highest photon energies (below 200 \AA). The reason for this discrepancy is not clear. The solid line through our data points represents a best fit to our data, which are tabulated in Table I.

A straight line extrapolation to zero of the first few data points yields an onset for double photoionization of 315 \AA or 39.4 eV . The accuracy of the relative cross sections is about $\pm 5\%$. This gives a maximum error in the extrapolation of $\pm 1 \text{ \AA}$ or $\pm 0.12 \text{ eV}$. Previous experimental values quote $39.3 \pm 0.5 \text{ eV}$ using double charge transfer spectroscopy²³, $39.8 \pm 0.3 \text{ eV}$ by use of electron impact techniques²⁴ and 40.1 eV from Auger electron spectroscopy²⁵. The theoretical value obtained by Hurley²⁶ was 38.1 eV .

Absolute branching ratios and relative cross sections were obtained for O^+ and N^+ ions as previously described. The relative cross sections were normalized to the absolute data at 304 \AA and are shown in Fig. 3. We would expect the data below 300 \AA to be influenced by energy discrimination effects. However, these appear to be small on two accounts. Firstly, the solid line, representing the best fit to our O^+ and N^+ data below 300 \AA , required very little adjustment to allow the sum of the individual fragment cross sections to equal the total fragment cross sections. Secondly, the absolute cross sections obtained by Brion *et al.*¹² are in good agreement with our O^+ and N^+ cross sections. A maximum deviation of about 14% occurs for N^+ at the shortest wavelengths. This implies that the kinetic energies of the O^+ and N^+ fragment ions do not vary by much over this spectral range.

To analyze the dissociative ionization features we first refer to the potential energy diagram of NO^+ shown in Fig. 4. The vertical lines starting from the ground state of NO delineate the Franck-Condon region. Two possible dissociative pathways are shown producing energetic N^+ ions with predicted kinetic energies as indicated. Only a few of the electronic states are shown for clarity in the discussion to follow. The energies of the electronic and vibrational levels were taken from spectroscopic data and the photoelectron data of Edqvist *et al.*¹⁵ There has been some uncertainty in the assignment of the states at 21.72 eV and 22.73 eV. In Fig. 4 they are identified as $c^3\Pi$ and/or $B^1\Pi$ and $B'^1\Sigma^+$ and/or $B^1\Pi$, respectively. The and/or assignment is given in brackets in Fig. 4. In the present discussion these states will be described simply as the $c^3\Pi$ and $B'^1\Sigma^+$ states.

The first dissociative ionization limit of NO is predicted to occur at 20.124 eV (616.1 \AA) producing $O^+(4S)$ and $N(4S)$, whereas the second limit

occurs at 21.04 eV (589.3 Å) producing $N^+(3p)$ and $O(3p)$. This is in precise agreement with the observed thresholds for these ions, as shown in Fig. 3. Thus, we know that both O^+ and N^+ ions are produced immediately their respective thresholds are reached. For O^+ production the most likely mechanism would be transitions into the $5\Sigma^+$ repulsive state with subsequent dissociation. But a direct transition into the $5\Sigma^+$ state is spin forbidden. However, a large number of bound vibrational levels of electronic states of NO^+ (for example, $w^3\Delta$, $W^1\Delta$, and $A^1\Pi$ states) lie between 20.1 and 21.0 eV. These states could be perturbed by the presence of the repulsive portion of the $5\Sigma^+$ state causing predissociation.¹⁶ There are also several Rydberg series of neutral states in this energy region that converge to the $c^3\Pi$ state of NO^+ and which produce numerous absorption lines between 20- and 21 eV.^{17,18} From the work of Hertz et al.¹⁰ we know that resonance transitions into these states readily autoionize and predissociate into $O^+(4s)$. Two of these states are observed in the present O^+ data between 584 and 595 Å (see Fig. 3).

We have also measured the kinetic energy of the O^+ ion fragment produced by the He I line (584 Å) and found it to vary continuously between 0 and 0.5 eV.¹⁹ This is consistent with transitions into the $5\Sigma^+$ repulsive curve as shown in Fig. 4. Note, that the dashed portion of the $5\Sigma^+$ curve is hypothetical, although there are theoretical studies that indicate that it has a bound potential.¹⁶

At the $c^3\Pi$ and $B'^1\Sigma$ thresholds (21.73 eV and 22.73 eV, respectively) there is a sudden increase in the N^+ ion fragment cross section but not in the O^+ cross section. This implies that the c and B' states predissociate into the primary products $N^+(3p) + O(3p)$. If this is the case we would expect the kinetic energies of the N^+ ion fragments to be as follows:



These values agree with our previously measured ion fragment energies from NO.¹⁹ Both states have been seen in photoelectron spectroscopy^{15,20-22} with well defined vibrational structure observed from the B' state¹⁵. It is not clear if these states partially or completely predissociate.

Higher energy electronic states have been observed in photoelectron spectroscopy in the regions 26-35 eV and 37-48 eV.^{21,22} Predissociation of these states could partially account for some of the structure observed in the O⁺ and N⁺ curves. However, predissociation of NO²⁺ could also account for the peaks observed between 200 and 300 Å.

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TABLE I. Total and dissociative photoionization cross sections for NO
measured in Megabarns (10^{-18} cm^2) between 120 and 614 \AA .

	$\lambda(\text{\AA})$	$\sigma_{\text{f}}(\text{total})^{\text{a}}$	$\sigma(\text{NO}^+)$	$\sigma(\text{N}^+)$	$\sigma(\text{O}^+)$	$\sigma(\text{NO}^{++})$	$\sigma(\text{fragments})$
	613.7	24.45	24.36		.09		.09
	608.7	24.70	24.58		.12		.12
	603.7	25.00	24.81		.19		.19
	598.7	25.20	24.99		.21		.21
	593.8	25.40	25.07		.33		.33
	588.8	25.56	25.28	0.04	.24		.28
HeI	584.3	25.70	25.22	0.11	.37		.48
	583.8	25.72	25.33	0.10	.29		.39
	578.8	25.85	25.46	0.14	.25		.39
	573.8	26.00	25.61	0.17	.22		.39
	571.3	26.04	25.06	0.77	0.20		.98
	568.8	26.10	24.73	1.16	0.20		1.37
	558.8	26.25	24.67	1.42	0.16		1.58
	548.8	26.32	24.60	1.56	0.15		1.72
	538.8	26.38	24.53	1.66	0.18		1.85
	528.8	26.40	24.24	2.00	0.16		2.16
	518.8	26.35	23.81	2.36	0.19		2.54
	508.8	26.22	23.30	2.74	0.19		2.92
	498.8	26.05	22.79	3.06	0.20		3.26
	488.8	25.80	22.28	3.32	0.20		3.52
	478.8	25.47	21.78	3.50	.19		3.69
	468.8	25.05	21.20	3.66	.19		3.85
	458.9	24.55	20.39	3.97	.19		4.16
	448.9	23.90	19.62	4.13	.15		4.28

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Table I continued

	$\lambda(\text{\AA})$	$\sigma_i(\text{total})^a$	$\sigma(\text{NO}^+)$	$\sigma(\text{N}^+)$	$\sigma(\text{O}^+)$	$\sigma(\text{NO}^{++})$	$\sigma(\text{fragments})$
	438.9	23.04	18.60	4.27	.18		4.44
	428.9	22.15	17.79	4.15	.21		4.36
	418.9	21.37	16.87	4.23	.27		4.50
	408.9	20.60	16.12	4.16	.32		4.48
	398.9	19.90	15.39	4.11	.40		4.51
	388.9	19.20	14.59	4.10	.51		4.61
	383.9	18.80	14.27	3.98	.55		4.53
	378.9	18.40	13.89	3.94	.57		4.51
	368.9	17.57	13.29	3.65	.64		4.28
	358.9	16.75	12.63	3.38	.74		4.12
	348.9	16.12	12.01	3.30	.81		4.11
	350	16.17	12.05	----	----		4.10
	340	15.60	11.48	3.20	0.91		4.12
	330	15.02	10.90	3.10	1.02		4.12
	320	14.50	10.35	3.01	1.13		4.15
	310	14.00	9.82	2.93	1.25	.014	4.18
HeII	303.8	13.75	9.51	2.86	1.34	.033	4.24
	300	13.62	9.35	2.87	1.36	.043	4.27
	290	13.25	8.90	2.84	1.44	.074	4.35
	280	12.87	8.47	2.83	1.47	.104	4.40
	270	12.50	8.00	2.85	1.48	.130	4.50
	260	12.10	7.46	2.87	1.50	.149	4.64
	250	11.48	6.92	2.77	1.52	.158	4.56
	240	10.60	6.35	2.58	1.51	.156	4.25

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Table I continued

$\lambda(\text{\AA})$	$\sigma_{\text{f}}(\text{total})^{\text{a}}$	$\sigma(\text{NO}^+)$	$\sigma(\text{N}^+)$	$\sigma(\text{O}^+)$	$\sigma(\text{NO}^{++})$	$\sigma(\text{fragments})$
230	9.74	5.80	2.40	1.38	.148	3.94
220	8.85	5.22	2.22	1.15	.139	3.63
210	8.00	4.68	2.03	0.98	.129	3.32
200	7.20	4.17	1.86	0.93	.118	3.03
190	6.58	3.67	1.70	0.92	.107	2.91
180	5.90	3.17	1.55	0.90	.103	2.73
170	5.25	2.70	1.38	0.85	.102	2.55
160	4.60	2.30	1.23	0.68	.087	2.30
150	4.00	1.97	----	----	----	2.03
140	3.35	1.70	----	----	----	1.65
130	2.85	1.43	----	----	----	1.42
120	2.40	1.20	----	----	----	1.20

^a C.E. Brion, private communication.

FIGURE CAPTIONS

1. Partial photoionization cross sections for NO^+ and total fragmentation (O^+ , N^+ , and NO^{2+}) as a function of wavelength. ●, present data (TOF mass spectrometer); ○, present data (magnetic mass spectrometer.) The solid line represents the recommended values and are tabulated in Table I.
2. Partial photoionization cross sections for NO^{2+} as a function of wavelength. ●, present data obtained with the magnetic mass spectrometer; ○, Brion et al.¹²
3. Partial photoionization cross sections for N^+ , O^+ , and NO^{2+} as a function of wavelength. ●, present data (TOF mass spectrometer); ○, present data (magnetic mass spectrometer); X, Brion et al.¹²
4. Simplified potential energy diagram for NO^+ . The area between the vertical lines represents the Franck-Condon region. The indicated transitions to the $\text{N}^+(3p)$ level represent the kinetic energies expected for the N^+ fragment ion. The position of the solid portion of the 5Σ curve is predicted from the observed kinetic energy of O^+ ions produced by 584 Å radiation (ref. 19).







