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KINETIC ENERGIES OF FRAGMENT IONS PRODUCED
BY DISSOCIATIVE PHOTOIONIZATION OF NO

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ABSTRACT

The kinetic energies of ions produced by dissociative photoionization of NO have been measured at the discrete resonance lines of He (584\AA) and Ne (736\AA), and with undispersed synchrotron radiation. O^+ ions were identified with energies from 0 to approximately 0.5 eV and two groups of N^+ ions one with energy of 0.36 eV and another with energies between 0.9 and 1.5 eV, apparently produced by predissociation of the $c^3\Pi$ and $B'^1\Sigma$ states, respectively.

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Introduction

A limited number of studies have been made of the kinetic energies of ion fragments produced by the process of dissociative photoionization, especially near the ionization threshold for these processes [1-4]. The information derived from such experiments is very important in developing potential energy curves or locating repulsive curves that perturb stable electronic states causing predissociation.

Studies have been made of the unimolecular dissociation of $(\text{NO}^+)^*$ where the excited NO^+ states were produced in ion sources by electron bombardment [5-7]. Energy resolved spectra of the O^+ fragments showed ion peaks at energies between 0.037 and 0.354 eV [5]. The peak energies were in good agreement with the extrapolated vibrational data of Edqvist et al. [8] for the $w^3\Delta$, $W^1\Delta$, and $A'^1\Sigma^-$ states of NO^+ , implying predissociation of some of these states.

The present work describes the first measurement of the kinetic energies of ion fragments produced directly by dissociative photoionization of NO .

Experimental

Photoionization of NO was produced by the 584\AA resonance line of He and by the 736\AA resonance line of Ne in order to study low energy O^+ ions created near the threshold for dissociative photoionization. The He and Ne light sources were used with a normal incidence monochromator to insure spectral purity. More energetic ions particularly N^+ were produced from higher lying excited states of NO by use of synchrotron radiation from the

Stoughton storage ring in Wisconsin. Because of the weak signals encountered preliminary measurements were made by using the zero order spectrum from a grazing incidence monochromator. The integrated spectrum produced radiation of all energies up to about 100 eV.

The gas jet and photon beam crossed at the center of a cylindrical ion chamber, producing the majority of the ions in a small central region. The directed motion of the molecules in the jet effectively prevented NO^+ ions and low energy fragment ions (< 0.1 eV) from escaping through the exit aperture of the ion chamber. The NO^+ ions that were observed came from the low general background pressure of NO that permeated the ion chamber. This provided excellent suppression of the NO^+ peak, thereby, allowing the low intensity ion fragments to be more readily resolved. The ions were formed in a field-free region and allowed to drift through an exit aperture. They were then accelerated or decelerated to match the fixed pass energy of the analyzer and subsequently were detected with a channel electron multiplier. The lens action produced by the acceleration/deceleration field had a large effect on the transmission efficiency of ions of different energies. Essentially, the greater the acceleration field the better the transmission of the higher energy ions.

The energies of the ions were measured with a 90° sector cylindrical energy analyzer, which had an energy resolution of about 0.5%. The contribution of the doppler effect, caused by the random motion of the parent ion, was minimized somewhat by using a molecular jet.

Although a mass spectrometer was not used with these exploratory measurements the identification of the major ions are not too ambiguous. Certainly, future work should use mass analysis for finer understanding of the ion energy results.

Results and Discussion

A potential energy diagram of NO^+ is shown in fig. 1. Only a few of the electronic states are shown for clarity in the discussion to follow. The energies of the electronic and vibrational levels are taken from spectroscopic data and the photoelectron data of Edqvist et al.[8]. There has been some uncertainty in the assignment of the states at 21.72 eV and 22.73 eV. In fig. 1 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. 1. 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 occurs at 20.124 eV producing $\text{O}^+(^4\text{S})$ and $\text{N}(^4\text{S})$, whereas the second limit occurs at 21.04 eV producing $\text{N}^+(^3\text{P})$ and $\text{O}(^3\text{P})$. Both thresholds can be reached by the 584\AA line (21.21 eV) but not by the 736\AA line (16.85 eV). We know that both O^+ and N^+ ions are produced immediately their respective thresholds are reached [9-11] and we have measured the absolute cross sections for producing NO^+ , O^+ , and N^+ at 584\AA [9,10]. These are, respectively, 25.2 Mb, 0.37 Mb, and 0.11 Mb ($1 \text{ Mb} = 10^{-18} \text{ cm}^2$).

Figures 2 (a) and (b) show the ion kinetic energy spectra produced by the 736\AA and 584\AA lines. The ions were accelerated to 37 eV, which gave an energy resolution of about 230 meV (this includes the effect of the Maxwell-Boltzmann distribution). With this resolution the zero of the energy scale is effectively located at the NO^+ maximum. The counting time for each peak was normalized to the same value of the product of the light intensity and the ionization cross section at each wavelength. The high energy tail on the 736\AA NO^+ data (fig. 2a) is a characteristic of our energy analyzer and is caused by ions scattered inside the analyzer. For

example, identical structure can be seen on Ar^+ ion peaks. However, in fig. 2(b) the 584\AA data shows a definite fragment ion superimposed on the instrumental tail. Thus, by subtracting the two spectra we obtain the true spectrum of the fragment ion. This result is shown in fig. 2(c). We can identify this ion as primarily O^+ because the N^+ ions are produced with energies between 0 and 90 meV and are thus effectively lost because of the jet-action of the gas beam. This would also apply to that portion of the O^+ signal. Furthermore, the cross section for N^+ production at 584\AA is about a factor of three less than O^+ . The true ratio of $\text{NO}^+ : \text{O}^+$ at 584\AA is 68:1. From figs. 2(a) and 2(c) the observed areas give a ratio of only 1.6:1. This shows the effectiveness of the jet-action in discriminating against the parent NO^+ ions. From the potential energy diagram in fig. 1 we would expect the O^+ energy to range between 0 and 0.5 eV. Allowing for the instrumental resolution and the high energy tail that must accompany each peak the observed spread between 0 and 1.0 eV is reasonable.

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 [12]. From the peak position of the data shown in fig 2(c) the $5\Sigma^+$ state should cross the center of the Franck-Condon region at about 20.6 eV or less. 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 [12]. The positioning of the repulsive portion of the $5\Sigma^+$ state agrees with the continuous production of O^+ ions that are observed in the mass spectrum of NO at all photon energies greater than 20.124 eV [9-11]. There are also several Rydberg series of neutral states in this energy region that converge to the $c^3\Pi$ (or $B^1\Pi$)

state of NO^+ and produce numerous absorption lines between 20 and 21 eV [13,14]. From the work of Hertz et al. [11] we know that resonance transitions into these states readily autoionize and predissociate into $\text{O}^+(^4\text{S})$.

For higher photon energies, using synchrotron radiation, a more complex energy spectrum is produced. A typical spectrum is shown in fig. 3. Because the zero order photon spectrum was used photons of all energies less than 100 eV were present. Again, the ions were accelerated to 37 eV. Thus, the resolution and focusing conditions were similar to that used for the data in fig. 2. We would expect, therefore, that the main NO^+ peak and the low energy $\text{O}^+(^4\text{S})$ continuum would be similar to that produced by the 584Å line in fig. 2(b). However, because the undispersed radiation would have a high percentage of low energy photons it is reasonable to expect a somewhat higher ratio of NO^+ to $\text{O}^+(^4\text{S})$ than observed at 584Å. The dashed line in fig. 3 is an estimate of the contribution of NO^+ and $\text{O}^+(^4\text{S})$ ions to the energy spectrum. Subtracting this contribution leaves a single energy peak at 0.36 eV. The dotted line indicates the high energy instrumental tail of this peak (see discussion of fig. 2(a)). The 0.36 eV fragment ion can be identified as $\text{N}^+(^3\text{P})$ originating from predissociation of the $\text{c}^3\Pi$ state. This electronic state has been observed in photoelectron spectroscopy of NO [8] as a single peak ($v = 0$) with a small unresolved tail (tentatively assigned by Edqvist et al. as the $\text{B } ^1\Pi$ state). Thus, predissociation of this state should also yield an ion fragment with a narrow energy range. This is in agreement with the present results. The observed ion energy is in excellent agreement with the predicted value of 0.362 eV if predissociation occurs from the $\text{c}^3\Pi$ ($v = 0$) value into $\text{N}^+(^3\text{P}) + \text{O}(^3\text{P})$ as indicated in fig. 1.

The last remaining feature is a broad continuum that can be correlated with predissociation of the $B^1\Sigma$ state into $N^+(^3P) + O(^3P)$. In the photoelectron spectrum of NO, Edqvist et al. have completely resolved the vibrational structure of the $B^1\Sigma$ state from $v = 0$ to $v = 13$ lying between 22.727 eV and 23.756 eV. If these states are perturbed and predissociation leads to $N^+(^3P) + O(^3P)$ the N^+ fragment ions would have energies lying between 0.9 and 1.5 eV, as indicated in fig. 1. Allowing for the resolution of our instrument there is excellent agreement with the observed energies as shown in fig. 3.

Evidence for predissociation of the $c^3\Pi$ and $B^1\Sigma^+$ states comes from studies of the dissociative photoionization of NO [9-11]. The increase in the number of N^+ ions at the thresholds of the above states is very dramatic. No corresponding increase in O^+ occurs at these thresholds.

Although other ion groups of N^+ and O^+ may be present the primary energetic ions appear to come from three groups, namely, $O^+(^4S)$ ions with energies from 0 to 0.5 eV from predissociation via the $5\Sigma^+$ state, $N^+(^3P)$ ions with 0.36 eV energy, and an $N^+(^3P)$ group with energies from 0.9 to 1.5 eV produced by predissociation of the $c^3\Pi$ and $B^1\Sigma^+$ states, respectively.

Further work is in progress to obtain mass analysis of the ionic fragments as a function of photon energy and in tandem with energy analysis.

Acknowledgment

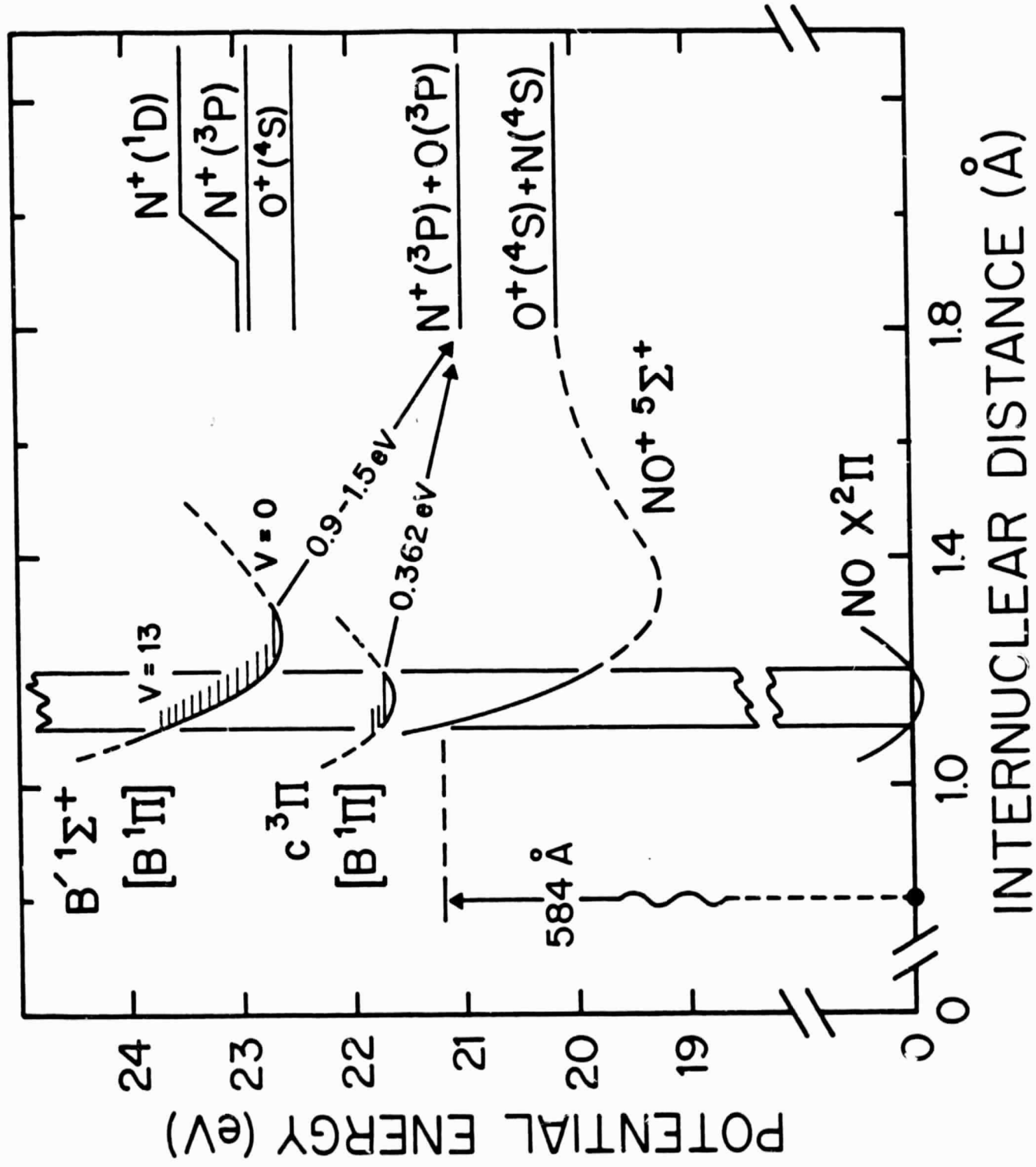
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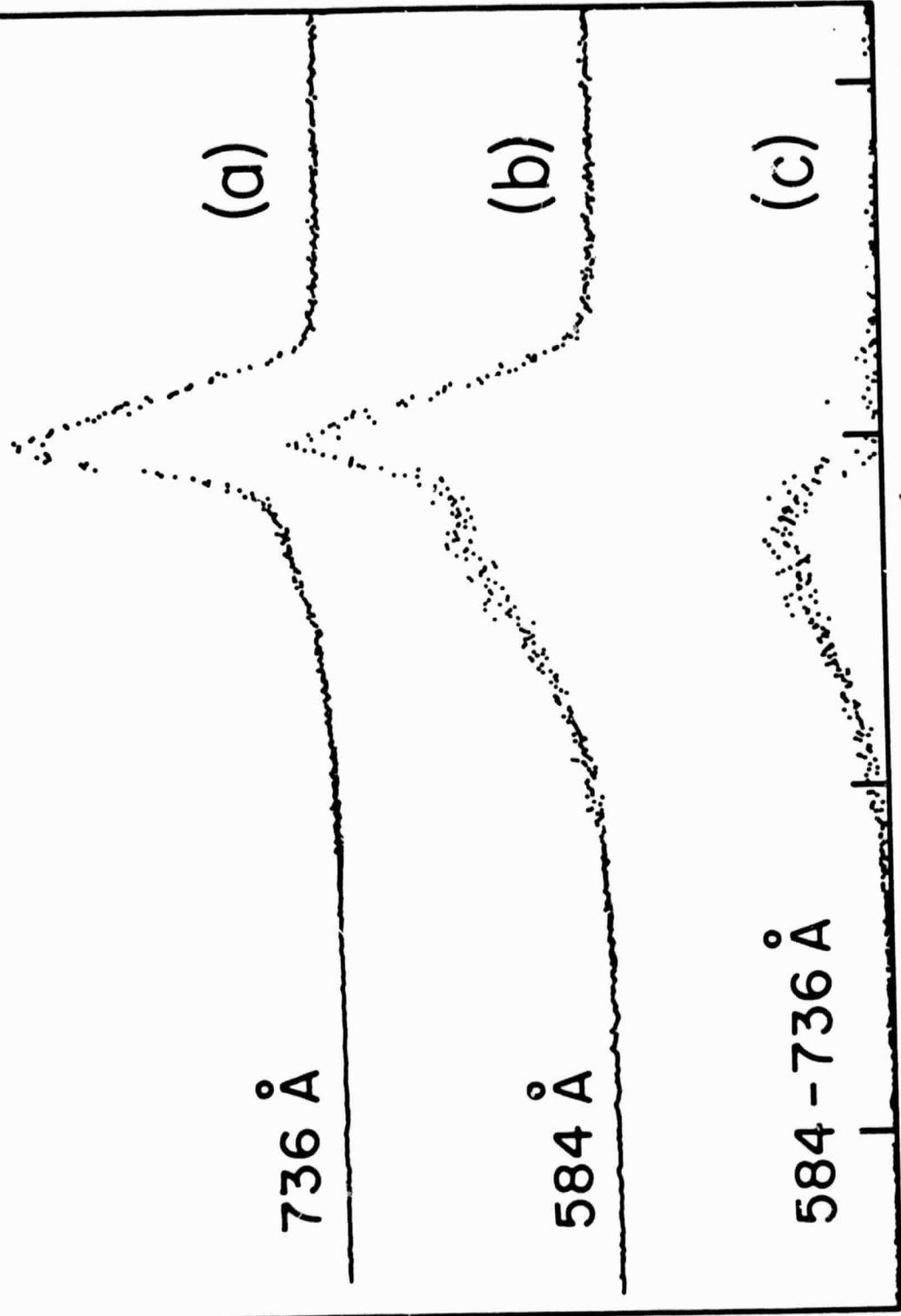
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FIGURE CAPTIONS

1. Potential energy diagram for NO^+ illustrating probable predissociation path-ways and suggested location of the repulsive portion of the $5\Sigma^+$ states (the depth of the potential well is purely schematic). The vertical lines represent the Franck-Condon region.
2. Ion kinetic energy spectrum from NO (a) produced by 736\AA radiation, (b) produced by 584\AA radiation and (c) energy of the O^+ fragment ion produced by subtracting the 736\AA energy spectrum from the 584\AA spectrum. Note, the high energy tail in (a) is instrumental.
3. Ion kinetic energy spectrum produced by dissociative photoionization of NO by undispersed synchrotron radiation. The dashed line extending from the main NO^+ peak is an estimate of the contribution of NO^+ and $\text{O}^+(^4\text{S})$ ions to the energy spectrum. The dotted line indicates an estimate of the high energy instrumental tail for the 0.36 eV peak.



ION COUNT RATE (arb. units)



(a)

736 Å

(b)

584 Å

(c)

584 - 736 Å

-1

0

1

2

ION ENERGY (eV)

