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Threshold Photoelectron-photoion Coincidence Imaging of Dissociation Dynamic of NO^+ at $c^3\Pi(v'=0)$ State

Jin-da Sun^a, Xiao-bin Shan^a, Fu-yi Liu^a, Liu-si Sheng^{a*}, Xiao-feng Tang^b, Ming-li Niu^b, Lei Song^b, Xiao-guo Zhou^b, Shi-lin Liu^b

a. School of Nuclear Science and Technology, National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China

b. Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

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The photodissociation of NO^+ at $c^3\Pi(v'=0)$ state is studied by threshold photoelectron-photoion coincidence imaging method. By some assumptions, the relations between velocity in center of mass (CM) coordinates and most probable center of mass (MPCM) coordinates, time of flight and displacement in the velocity map image of fragment ions are derived using vector addition of velocity and displacement on the condition of perpendicular molecular beam. Using these relations the velocity in CM coordinates, the velocity and angular distribution of N^+ fragment ions in MPCM coordinates are obtained and discussed, respectively.

Key words: Threshold photoelectron-photoion coincidence imaging, Velocity map imaging, Nitric oxide, Kinetic energy released distribution, Angular distribution

I. INTRODUCTION

The valence ionic NO^+ at $c^3\Pi(v'=0)$ state has been investigated by photoelectron spectroscopy (PES) [1, 2], photoion efficiency spectroscopy (PIE) [3], velocity imaging photoionization coincidence spectroscopy (VIPCO) [4], and photoelectron-photoion coincidence spectroscopy (PEPICO) [5].

Erman *et al.* studied the photoionization and photodissociation of NO in 9–35 eV energy range using synchrotron radiation, and predicted that the $c^3\Pi(v'=0)$ state NO^+ is predissociative to form the products of $\text{N}^+(^3\text{P})$ and $\text{O}(^3\text{P})$ [3]. Eland and Duerr studied the dissociation of NO^+ using PEPICO method and found the anisotropic oriented-molecule electron angular distribution and dissociation channel branching ratios at $c^3\Pi$ state of NO^+ , indicating that NO^+ at this state is fully dissociated to N^+ ions and O atoms [5]. The fixed-molecule angular distribution of photoelectron in ionization of NO to $\text{NO}^+(c^3\Pi)$ was extracted using VIPCO technique by Eland *et al.* [4].

In this work, we study a dissociation of $\text{NO}^+(c^3\Pi)$ using the newly developed threshold photoelectron-photoion coincidence (TPEPICO)-imaging apparatus [6]. The TPEPICO image of N^+ fragment ions from dissociation of state-selected $\text{NO}^+(c^3\Pi)$ presents for the first time. The speed and angular distribution of N^+

fragment ions in dissociation are directly derived from the recorded images.

II. EXPERIMENTS

The experiments were performed at the Atomic and Molecular Physics (U14-A) Beamline of National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The beamline and the TPEPICO-imaging instrument were described in detail elsewhere [6, 7] and here is a brief. The undulator-based U14-A beamline of 800 MeV electron storage ring consists of a 6-m monochromator, in which three gratings (370, 740, and 1250 grooves/mm respectively) are mounted. These three gratings have the photon energy ranges from 7.5 eV to 22.5 eV, 15 eV to 45 eV, and 36 eV to 124 eV respectively, and the energy resolving power ($E/\Delta E$) is up to 2000 when the entrance and exit slits are set to 80 μm . In this experiment only the 370 grooves/mm grating is used, and the wavelength is accurately calibrated by the photoionization spectrum of inert gases.

The TPEPICO-imaging apparatus is divided by a 0.5 mm diameter skimmer (Beam Dynamics) into two chambers, source chamber and detect chamber, which are pumped by turbo molecular pumps (KYKY FF-250/1800, Leybold T1600 respectively) backed with root pumps (Leybold WA251) and dry pump. The supersonic molecular beam is introduced through a homemade 30 μm diameter continuous nozzle which is fixed 25 mm upstream from the skimmer, and interacts perpendicularly with synchrotron radiation (SR)

* Author to whom correspondence should be addressed. E-mail: lssheng@ustc.edu.cn, Tel.: +86-551-3602021

at a position about 100 mm downstream from the nozzle. The dimension of the focus spot of SR is about $0.5\text{ mm}\times 1\text{ mm}$, and the estimated width of the MB along the propagation direction of SR is 3 mm, thus the volume of the ionization region is about $0.5\text{ mm}\times 3\text{ mm}\times 1\text{ mm}$. The ion optic lens, which is shielded by a 1 mm thick μ -metal tube in order to eliminate stray magnetic field, is mounted precisely so that its axis is perpendicular to the direction of flow of MB and propagation of SR.

The apparatus works at the mode of single-start/multi-stop. The threshold photoelectron is detected by MCP assembly, and the signal is magnified and transferred to P7888 (Fast Comtec, Germany) card as a start. The signals of photoions, which are mass selected and time sliced by adding a high voltage pulse on the front surface of the MCP and detected by the MCP assembly (Burle Industries, 40 mm diameter)/phosphor screen (Burle Industries, P20), are stops. The pulse's duration and delay time are set as 0.120 and 7.175 μs , respectively, which are optimized by pulse generator (DG535, SRS) to gate N^+ whose TOF spreads 567 ns. A 333 lpi metallic mesh is mounted in front of the ion detector to guarantee homogeneous potential field of free flight tube, and a 2 kV high DC relative to the potential of photoionization region is applied to the front surface of MCP in order to provide enough response efficiency of ion detector. Because there is only 1 mm distance between the mesh and MCP, the image distortion can be neglected. The TPEPICO image of fragment ions is recorded by a TE-cooling charge coupled device (CCD) camera (Andor, DU934N-BV). In our experiment the recorded image is accumulated for 2 h.

The 10% NO molecule seeded in He, with a backing pressure of 178 kPa, is introduced into the detecting chamber where the pressure becomes 22 μPa . Such expansion will generate the NO dimer whose concentration relative to monomer NO may be less than 1.2% obtained for pure NO molecules [8], and its dissociative photoionization (DPI) channel at 21.72 eV is unknown. Because of the small quantity of NO dimer in molecular beam, the N^+ dissociated from NO dimer ions are expected to contribute a little and almost all N^+ produced at this energy are processed as the production of the DPI of NO molecules.

In this experiment, we first measure the threshold photoelectron spectrum (TPES) of NO molecule around 21.7 eV to confirm the observed photoelectron peak of 21.72 eV as resonance of the $c^3\Pi$ state of NO^+ . Then we record the time-sliced TPEPICO image of N^+ with the selected mass gate at the photon energy of SR (21.72 eV). The count rate of threshold electrons at 21.72 eV was derived from the measured TPES as 432 counts/s, which varied a bit during the experiment because of the gradually decreased SR photo flux, while the coincidence count rate of N^+ can be estimated to be 268 counts/s from the coincident mass spectrum. Since the electron storage ring operates at multibunch

mode and the interval between each adjacent bunches is 5 ns, the total yield of ions are expected to be about 10^{-6} counts/pulse.

III. RESULTS AND DISCUSSION

The TPEPICO image of N^+ produced by dissociation of the $c^3\Pi$ ($v'=0$) state of NO^+ is shown in Fig.1. There are one ring corresponding to N^+ and a bright elliptic spot. The ring and the spot are all eccentric to the left along the direction of MB (x axis), because of the velocity of NO^+ and CM of the fragments, and of the difference of flight time between NO^+ (111.67 μs) and N^+ (7.59 μs), respectively. In addition, the bright elliptic spot looks very similar to the TPEPICO image of Ar^+ at 15.760 eV, which are contributed by the NO^+ coincidence with energetic photoelectrons [6]. There are moderate heteropic intensity of the observed image, *e.g.* intensity of the upper part of the ring are weaker than that of the bottom, which are due to the limited accumulation time. The polarization vector ε of SR is horizontal in the image as shown in Fig.1.

In traditional velocity map imaging, the relation between the velocity of ions v' and the radius of the ring R' can be described as [9]

$$R' = N \times v' \times t \quad (1)$$

where N is the magnification factor of the apparatus and t is the TOF of ion. Assuming the TOF of the fragment ions and their CMs is equal both in laboratory and CM coordinates, and it is reasonable when the fragment ions are mass-selected by applying a very short voltage pulse. Using Eq.(1) and vector addition of velocity and

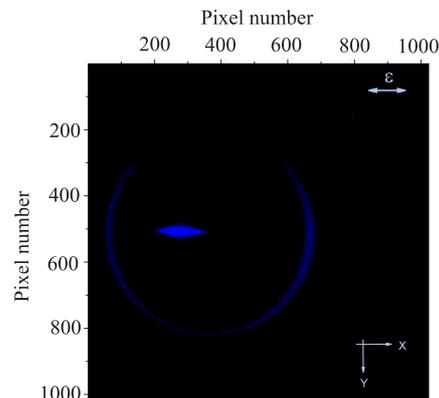


FIG. 1 The TPEPICO-VMI image of N^+ produced by dissociation of the $c^3\Pi(v'=0)$ state of NO^+ . The ring and the elliptic area which correspond to the N^+ and NO^+ caused by fault coincidence with energetic electrons, respectively, are eccentric to the left along the direction of the MB (x axis). The SR propagates along y axis and the polarization vector ε is horizontal in the image. For clarity, the reader can refer to the web version of this article.

displacement, the relation among the velocity \vec{v}_0 in CM coordinates, the TOF t and the displacement \vec{R}_{CM} of the ions in the image can be described as:

$$\vec{R}_{\text{CM}} = N \times \vec{v}_0 \times t \quad (2)$$

As the CM of fragments has the same velocity as that of parent ions, the center of the ring is just at the position where the MPCMs of fragments map to. From that fragment ions with most probable velocity flight away and hit the detector at the place where the peak of ring locates, the absolute value of \vec{R}_{CM} is equal to the radius of the ring R_0 , and the relation above can be rewritten as:

$$R_0 = N \times v_0 \times t \quad (3)$$

Similarly, the velocity distribution in MPCM coordinates can be described as:

$$R = N \times v \times t \quad (4)$$

where R is the displacement between the image of ions and the center of ring and v is the velocity of fragment ions in MPCM coordinates, respectively. Obviously, when $R=R_0$, Eq.(4) becomes Eq.(3).

The TOF of ions behaves as $t \propto \sqrt{m/qU}$ which is common in TOF spectrometry, where m is the mass of the ion, q is the charge of ions and U is the potential applied on ion optic lens. Substitution it in Eq.(3) gives

$$R_0 \propto N \sqrt{T_0/qU} \quad (5)$$

where T_0 is the kinetic energy released (KER) of the ions in CM coordinates.

The image of N⁺ in Fig.1 is processed using the Glass Onion software [10]. Because N⁺ is time sliced, the image is loaded as an "exiting inversion" file and the velocity profile, angular distribution and spatial anisotropic parameter are obtained directly without Abel inversion transform.

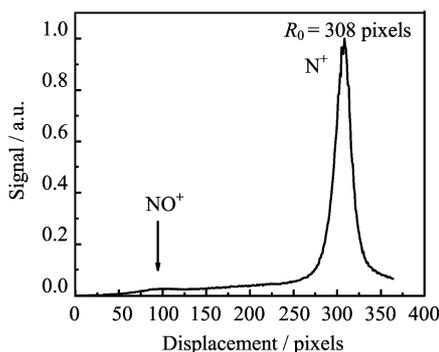


FIG. 2 Velocity distribution of ions with respect to pixels in MPCM coordinates. The pixel value ranges from 2100 to maximum. The lower peak at 94 pixels corresponds to NO⁺ ions caused by fault coincidence.

The velocity distribution of the ions with respect to pixels in MPCM coordinates is shown in Fig.2. The pixel value of image has a base of about 2100, and the profile shown in Fig.2 is obtained with pixel value ranges from 2100 to maximum. The peak at 94 pixels is contributed by the fault coincident NO⁺, while the peak at 308 pixels corresponds to the ring of image of N⁺ fragment ions. Using Eq.(5), the magnification factor of the apparatus, N , is calibrated with the TPEPICO image of O⁺ dissociated from $B^2\Sigma_g^-(v'=0)$ state of O₂⁺ in Ref.[6], then the kinetic energy of N⁺ in CM coordinates is obtained to be 0.423 eV, corresponding a velocity of 2.415 km/s. Thus the total KER which is the sum of the kinetic energy of the two kind of fragments, is 0.793 eV achieved by conversation of momentum and energy, and it agrees with the KER of 0.689 eV calculated by photon energy (21.72 eV) and the first dissociation limit (21.031 eV) [5] with dissociation product of N⁺(³P) and O(³P). The 0.104 eV discrepancy means a deviation of 21 pixels of R_0 , which is equal to the full width at half maximum (FWHM) (21 pixels) of the velocity profile of N⁺, and less than zero point energy of NO molecule ($\omega_e=1904.204$ or 1904.04 cm⁻¹) [11].

Figure 3 shows the angular distribution of N⁺ from in MPCM coordinates with the velocity (displacement) in the range of FWHM in Fig.2. The distribution is fitted by the Eq.(6),

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi[1 + \beta P_2(\cos\theta)]} \quad (6)$$

where $P_2(\cos\theta)$ is the second-order Legendre polynomial, θ is the angle between the velocity vector of N⁺ and the polarization vector of SR, σ is the partial cross section, and β is the constant describing the anisotropy of distribution. Thus the value of β in this work is estimated as 0.683 ± 0.056 from global fitting the angular distribution in Fig.3.

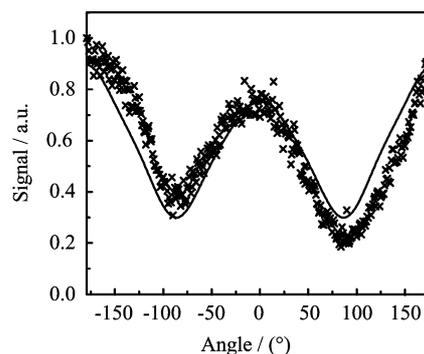


FIG. 3 Angular distribution of N⁺ in MPCM coordinates with the velocity in the range of FWHM in Fig.2. "x" denotes the measured distribution, and solid line denotes the fit by the Eq.(6).

IV. CONCLUSION

By some approximations, the relation between the velocity v_0 in CM coordinates, TOF t and radius of the ring R_0 of ions in velocity map imaging on the condition of perpendicular MB can be described as $R_0 = N \times v_0 \times t$, alternatively can be written as $R_0 \propto \sqrt{NT_0/qU}$. The velocity of ions in MPCM coordinates can be described as $R = N \times v \times t$.

The TPEPICO-imaging of N^+ produced by the dissociation of NO^+ at the state of $c^3\Pi(v'=0)$ is studied. The speed of N^+ in CM coordinates obtained using the equations above is 2.415 km/s, corresponds a kinetic energy of 0.423 eV and KER of 0.793 eV, indicating that the $c^3\Pi(v'=0)$ state NO^+ fully predissociates to $N^+(^3P)$ and $O(^3P)$ which agrees with the conclusion get by other methods [3, 5]. The dissociation process presents an obvious anisotropy, and the value β obtained by fitting the angular distributon of N^+ ions in MPCM coordinates is 0.683 ± 0.056 which must be more accurate.

V. ACKNOWLEDGMENTS

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(No.10979042).

- [1] O. Edqvist, E. Lindholm, L. E. Selin, H. Sjögren, and L. Åsbrink, *Ark. Fys.* **40**, 439 (1970).
- [2] O. Edqvist, L. Åsbrink, and E. Lindholm, *Z. Naturforsch. A* **26**, 1407 (1971).
- [3] P. Erman, A. Karawajczyk, E. Rachlewkaline, and C. Stromholm, *J. Chem. Phys.* **102**, 3064 (1995).
- [4] J. H. D. Eland, M. Takahashi, and Y. Hikosaka, *Faraday Discuss.* **115**, 119 (2000).
- [5] J. H. D. Eland and E. J. Duerr, *Chem. Phys.* **229**, 1 (1998).
- [6] X. F. Tang, X. G. Zhou, M. L. Niu, S. L. Liu, J. D. Sun, X. B. Shan, F. Y. Liu, and L. S. Sheng, *Rev. Sci. Instrum.* **80**, 113101 (2009).
- [7] S. S. Wang, R. H. Kong, X. B. Shan, Y. W. Zhang, L. S. Sheng, Z. Y. Wang, L. Q. Hao, and S. K. Zhou, *J. Synchrotron Radiat.* **13**, 415 (2006).
- [8] C. Y. Ng, P. W. Tiedemann, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.* **66**, 3985 (1977).
- [9] A. T. J. B. Eppink and D. H. Parker, *Rev. Sci. Instrum.* **68**, 3477 (1997).
- [10] S. Manzhos and H. P. Looock, *Comput. Phys. Commun.* **154**, 76 (2003).
- [11] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*, 2nd edn., New York: Van Nostrand Reinhold Company, 476 (1979).