

## Asymmetry of Departing Fragment Ion in the $K$ -Shell Excitation of $N_2$

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(Received 29 July 1988)

The angular distribution of departing  $N^+$  ions from  $N_2$  stimulated by  $K$ -shell photoexcitation has been measured by use of a time-of-flight mass spectrometer. A detailed analysis of the flight-time spectra shows that at 401 eV, i.e., the resonance transition from  $1s\sigma_u$  to  $2p\pi_g$ , the asymmetry parameter  $\beta$  is close to  $-1$ . Between 405 and 410 eV,  $\beta$  shows an oscillatory variation due to the core-electron excitations to the Rydberg states. In the  $\sigma_u$ -type shape resonance,  $\beta$  is larger than 0. The results obtained are discussed in relation to the characteristics of the  $K$ -shell excited states.

PACS numbers: 33.80.Eh, 33.80.Gj, 33.90.+h

A core electron in a molecule is excited to unoccupied valence orbitals, to Rydberg orbitals, and to shape resonances in the continuum by soft x-ray irradiation. Regarding  $N_2$ , photoabsorption spectra using synchrotron radiation<sup>1,2</sup> and electron energy-loss spectra<sup>3-5</sup> show fine structure near the  $K$  edge. The strong peak of the  $1s\sigma_u \rightarrow 2p\pi_g$  transition appears at 401 eV. Above this energy, there are several peaks caused by excitations of a core electron to discrete Rydberg orbitals. Above the inner-shell ionization threshold at 409.9 eV, a larger band can be seen, consisting of a shape resonance peaking at 419 eV and two doubly excited states with peaks at 414 and 415 eV. Several theoretical studies on  $K$ -shell spectra of  $N_2$  have been carried out.<sup>6-11</sup> Dehmer and Dill<sup>6</sup> have reported the partial cross sections of inner-shell photoionization for the four dipole-allowed channels, calculated using a multiple-scattering model. They explained that the shape resonances arise from centrifugal-barrier effects in high- $l$  components of the final-state wave function.

When a diatomic molecule is excited into a discrete molecular orbital by linearly polarized light, the excited molecule has a certain orientation. This is true even in the continuum, where some orientations may occur at energies corresponding to shape resonances or because of the difference of oscillator strengths between the overlapping final states. The molecule is selectively excited in the molecular orientation parallel to the electric vector of the photon when the transition takes place from the  $\Sigma$  state to the  $\Sigma$  state. The excitation occurs selectively in the molecular orientation perpendicular to the electric vector when the transition takes place from the  $\Sigma$  state to the  $\Pi$  state. These orientations are closely connected to the angular distribution of emitted electrons<sup>12,13</sup> and/or of dissociating fragments.<sup>14,15</sup>

Dissociation of  $N_2$  following  $K$ -shell excitation has been extensively studied in recent years.<sup>16-21</sup> Eberhardt *et al.* have measured the intensity ratios of the fragment ions ( $N^+$  and  $N^{++}$ ) and  $N_2^+$  using a time-of-flight (TOF) mass spectrometer.<sup>16</sup> They have also clarified the dissociation pathways using an Auger-electron-

photoion coincidence technique.<sup>17</sup> The present authors have measured the kinetic-energy distribution of  $N^+$  and  $N^{++}$  fragment ions by using a TOF mass spectrometer in a photoelectron-photoion coincidence mode<sup>18,19</sup> and in a photoion-photoion coincidence mode.<sup>20</sup> The present study shows the angular distribution of the  $N^+$  ions from  $N_2$  in the decay of the inner-shell vacancy.

The experiments were performed with a new beam line consisting of a grasshopper monochromator with a resolution of about 0.8 eV at 400 eV, which was installed at the electron storage ring TERAS<sup>22-24</sup> at the Electro-technical Laboratory. The measurements were carried out with use of the TOF mass spectrometer, which can be rotated in the plane perpendicular to the photon beam. The TOF mass spectrometer previously used<sup>18-20</sup> was revised so as to be rotatable for this study. The experimental setup will be described in detail elsewhere.<sup>25</sup> The TOF mass spectrometer was operated in the photoelectron-photoion coincidence mode. The relative photon flux was monitored by an electron beam monitor at the ring and by a ceramic channeltron behind the TOF spectrometer.

When a fragment ion has some angular distribution, the TOF spectrum depends on the angle ( $\theta$ ) between the TOF spectrometer axis and the polarization vector of the incident photon beam. The flux of the dissociated fragment ions along a solid angle  $\Omega$  can be expressed by Eq. (1) with an asymmetry parameter  $\beta$ <sup>14,15</sup>:

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

When all the dissociating ions reach the ion detector (this means that the ion collection efficiency is 100%), the profile of the TOF spectrum of ions with only one kinetic energy is expressed as

$$f(t) = \frac{1}{4} \sigma_t (2 + \frac{1}{2} \beta (1 - 3 \cos^2 \theta) \{1 - 3 [(t - t_0)/\Delta t]^2\}), \quad (2)$$

for  $t_0 - \Delta t < t < t_0 + \Delta t$ , where  $t$ ,  $t_0$ , and  $\Delta t$  denote the flight time of the ion with kinetic energy, the flight time

of the ion with no kinetic energy, and half the width of the TOF spectrum derived from the kinetic energy, respectively. From Eq. (2), the TOF spectrum is exactly independent of  $\beta$  at the magic angle of  $54.7^\circ$ , when the ion collection efficiency is 100%. Even when the ion collection efficiency is not 100%, the TOF spectrum changes at most by 1% as  $\beta$  changes from  $-1$  to  $2$ . This fact has been confirmed by a simulation calculation.<sup>25</sup>

The effect of an accelerating field in the interaction region might be expected to modify the value of  $\beta$ . Thus, two separate values of the electric field, 13 and 26 V/mm, were applied at the interaction region in the spectrometer in order to confirm that the measured values of  $\beta$  were independent of the electric field (see Refs. 19 and 25 for details). The angles used in the measurements were  $0^\circ$ ,  $30^\circ$ ,  $54.7^\circ$ , and  $90^\circ$  for the same reason.

Figure 1 shows the TOF spectra of  $N^+$  ions at 392.0 eV (valence ionization), 401.0 eV ( $1s\sigma_u \rightarrow 2p\pi_g$  resonance), 406.1 eV ( $1s\sigma_u \rightarrow 3s\sigma_g$ ), 409.9 eV ( $K$ -shell ionization threshold), and 418.9 eV ( $\sigma_u$ -type shape resonance) taken at  $0^\circ$  and  $90^\circ$ . The central sharp peak corresponds to doubly charged molecular ions which have no kinetic energy. The two peaks at both sides of the central peak arise from  $N^+$  ions released with kinetic energies. When the molecule dissociates only in the orientation parallel to the axis of the TOF spectrometer, the intensity at the central part of the TOF spectrum decreases and that at both sides increases. When the molecule dissociates only perpendicularly to the axis, the central part comes up and both sides go down. For example, both side peaks of the TOF spectrum at 401 eV taken at  $90^\circ$  become large in comparison with those taken at  $0^\circ$ . This shows that the molecule preferentially dissociates perpendicularly to the electric vector of the photon at 401.0 eV. On the other hand, the features of the profiles

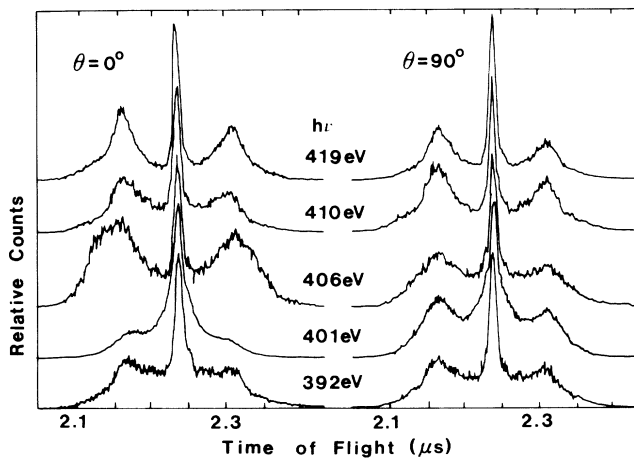


FIG. 1. TOF spectra of  $N^+$  at 392.0, 401.0, 406.1, 409.9, and 418.9 eV at the angles of  $0^\circ$  and  $90^\circ$ . The angle is measured between the TOF spectrometer axis and the polarization direction of the photon.

of the TOF spectra at 406.1 eV is contrary to these at 401.0 eV. This result indicates that the molecule preferentially dissociates in the orientation parallel to the electric vector.

In order to determine the asymmetric parameter  $\beta$  from the angle-dependent TOF spectra, we have used the following procedure. The TOF spectrum is determined by the kinetic-energy distribution and the angular distribution of the dissociating ion, the geometrical orientation of the TOF mass spectrometer, and the applied electric fields. The latter two factors are set at fixed values in the measurements. The undetermined factor necessary for derivation of the angular distribution is the kinetic-energy distribution of the fragment ion. Fortunately, even if the molecule dissociates with any value of the asymmetry parameter, the TOF spectrum of the fragment ion taken at the magic angle of  $54.7^\circ$  is the same as that of the isotropic dissociation ( $\beta=0$ ). Then the kinetic-energy distribution is determined from the TOF spectrum at  $54.7^\circ$  by the simulation calculation assuming that  $\beta=0$ . This method was described in detail previously.<sup>19</sup> Next, with the determined kinetic-energy distribution, the TOF spectra taken at  $0^\circ$ ,  $30^\circ$ , and  $90^\circ$  are simulated by the calculation with the assumption of various  $\beta$  values. In this calculation, the photon is assumed to be 100% linearly polarized. The  $\beta$  value is determined

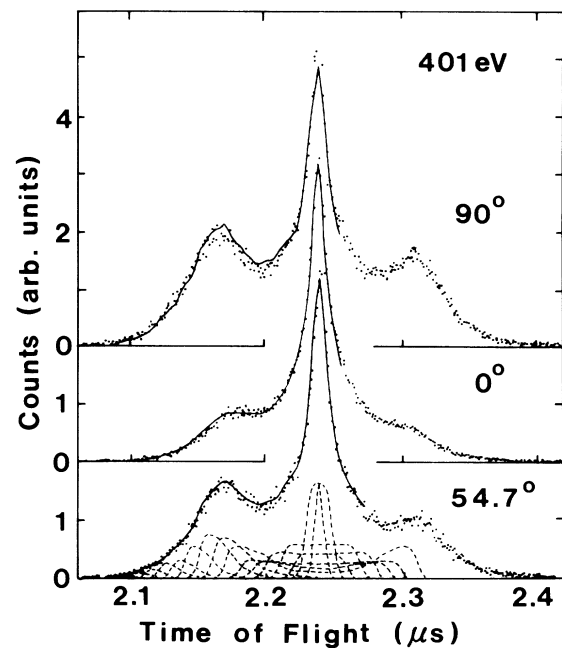


FIG. 2. TOF spectra of  $N^+$  at 401.0 eV measured at  $54.7^\circ$ ,  $0^\circ$ , and  $90^\circ$  from bottom to top. Dots are the experimental data. Broken curves are the profiles derived from the simulation calculation on the assumption that  $\beta = -0.7$  and the kinetic energies of  $N^+$  are 0, 0.059, 0.24, 0.53, 0.94, 1.47, 2.11, 2.88, 3.76, 4.75, 5.87, 7.10, 8.45, 9.92, 11.5, and 13.2 eV, from inner to outer. Solid curves are the sum of the broken curves.

so as to minimize the difference between the experimental data and the calculated profile.

Figure 2 shows examples of the TOF spectra obtained by this fitting procedure, where the results are represented for  $N^+$  at 401 eV with the assumption that  $\beta = -0.7$  at the angles of  $54.7^\circ$ ,  $0^\circ$ , and  $90^\circ$ . Dots are the experimental points. Broken curves in the bottom are the calculated profiles with kinetic energies of 0, 0.059, 0.24, 0.53, 0.94, 1.47, 2.11, 2.88, 3.76, 4.75, 5.87, 7.10, 8.45, 9.92, 11.5, and 13.2 eV from inner to outer. The solid curves are the sum of the broken curves. At  $0^\circ$  and  $90^\circ$ , only solid curves are drawn. When the nitrogen molecular ion dissociates into  $N^+$  and  $N^+$ , one of the  $N^+$  ions reaches the detector faster than the other. If the ion collection efficiency is not small, the signal derived from the  $N^+$  ion reaching the detector faster becomes higher than the other. For this reason, the calculated profiles were fitted to the left-hand side of the experimental data.

Figure 3 shows the asymmetry parameter  $\beta$  (lower panel) and the yield of the total electron signal (upper panel) both measured with the same photon energy resolution. The yield spectrum indicates the transitions to the Rydberg states in a clearer manner than the previous studies.<sup>16,18-21</sup> The asymmetry parameter has an oscillatory variation due to the characteristics of the different excited states. At peak A (401.0 eV,  $1s\sigma_u \rightarrow 2p\pi_g$ ),  $\beta$  is close to  $-1$ , which is consistent with that expected for

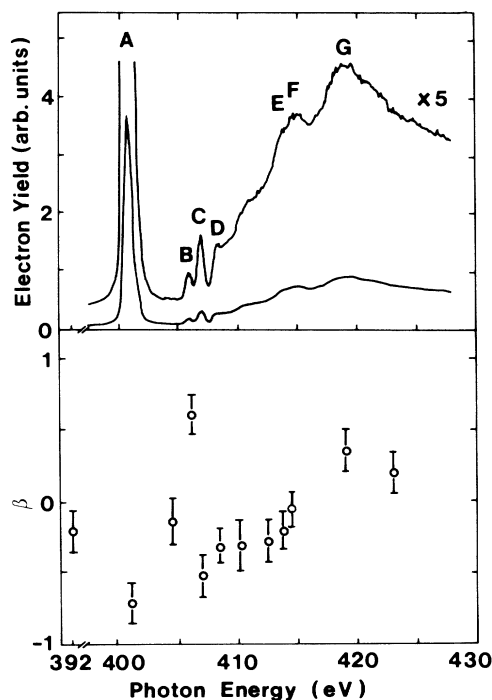


FIG. 3. Asymmetry parameter of departing  $N^+$  and the yield of the total electron signal as a function of photon energy. A-G were inserted for clarity of discussion in the text. Bars indicate the size of uncertainty.

this type of transition ( $\Sigma \rightarrow \Pi$ ). This fact postulates that the present analysis is adequate and free from any large systematic error. A slight deviation of  $\beta$  from  $-1$  probably originates from the following possibilities. First, the dissociation is not so fast compared to the molecular rotation. Second, the polarization degree of the photon is not 100%. Finally, below this photon energy, only valence electrons can be excited. However, because the  $N^{++}$  ion is observed, it must be caused by a double valence ionization.<sup>25</sup>  $\beta$  is about  $-0.2$  in this region. These transitions should exist as the background of the spectra at other photon energies.

At peak B (406.1 eV,  $1s\sigma_u \rightarrow 3s\sigma_g$ ),  $\beta$  is about 0.6. The  $\beta$  value is expected to be 2 from this transition. Because the background from the valence ionization at this energy is about 55% however,  $\beta$  is expected to decrease to 0.8. The remaining difference, 0.2, probably comes from the same reasoning that applies at 401 eV. At peak C (407.0 eV,  $1s\sigma_g \rightarrow 3p\pi_u$  and  $3p\sigma_u$ ),  $\beta$  is about  $-0.55$ . According to the work by Dehmer and Dill,<sup>6</sup> the partial cross section of the excitation to  $3p\pi_u$  is larger than that to  $3p\sigma_u$ . Thus the value obtained here is reasonable. At peak D (408.4 eV,  $1s\sigma_u \rightarrow 3d\pi_g$ ,  $3d\sigma_g$ , or  $4s\sigma_g$ ),  $\beta$  is about  $-0.3$ . This means that the oscillator strength to  $\pi_g$  is stronger than that to  $\sigma_g$ , which is in agreement with the theoretical prediction.<sup>6</sup> From peak D to peak G (shape resonance),  $\beta$  gradually increases and reaches about 0.3. This is consistent with the prediction that the cross section of the  $1s\sigma_g$  to  $\sigma_u$  transition becomes largest at point G, at 418.9 eV, by a  $\sigma_u$ -type shape resonance.<sup>6,7</sup> Doubly excited states at the peaks of E and F do not contribute considerably to the value of  $\beta$ . This is probably because the orientation of the molecule does not have an appreciable effect on the transition involving two electrons.

In conclusion, we have obtained the asymmetry parameter for the departing fragment ion induced by the anisotropic  $K$ -shell photoexcitation of a free molecule. It was found that the dissociating-ion anisotropy strongly depends on the excited state of  $N_2$ . The shape resonance was clearly demonstrated to be  $\sigma_u$  type. The measurement of the asymmetry of ion dissociation has been shown to be a powerful tool for determining the symmetry of the excited states.

We wish to express our sincere thanks to the members of the accelerator group of the Electrotechnical Laboratory for providing synchrotron radiation. We are grateful to Dr. S. Abe and Dr. U. Becker for fruitful comments. We are indebted to Professor J. A. R. Samson and Dr. N. Takata for critical readings of the manuscript.

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