

**Angular Distributions of Molecular Photofragments Emitted following  $K$ -Shell Excitation of  $N_2$** 

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Angle-resolved photoion spectroscopy has been applied for the first time to molecular fragments emitted after Auger decay following photoexcitation of the  $N_2$   $K$  shell in the gas phase. Considerable angular distribution asymmetries of photofragments have been observed not only at the  $\pi^*$  discrete resonance but also across the  $\sigma^*$  shape resonance.

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The  $K$ -shell excitation spectra of first-row diatomic molecules show a wealth of spectroscopic detail in the region around the onset of  $K$ -shell ionization.<sup>1</sup> This structure has mainly been assigned to promotions of a  $K$ -shell electron into unoccupied valence and Rydberg states and into the continuum. The broad enhancement in the near continuum of these spectra arises from the shape of the molecular potential experienced by the photoelectron when it leaves the molecule: Therefore, this phenomenon is referred to as shape resonance.<sup>2</sup> Photoexcitation into the discrete states produces neutral molecular excited states with definite, characteristic orientations, because the excited states have definite symmetries. Photoionization into the shape resonance produces molecular ions with energy-dependent orientations characteristic of each resonance,<sup>3</sup> because the shape resonance enhances photoabsorption along the characteristic direction of the molecule.<sup>2</sup> To name typical examples of these two types of photoexcitation, there is a  $1\sigma \rightarrow \pi^*$  intense discrete resonance and a  $1\sigma \rightarrow \sigma^*$  shape resonance in  $N_2$ . As a consequence of the dipole selection rules, the photoabsorption to the  $\pi^*$  excited state preferentially yields excited molecules with orientation perpendicular to the electric vector of the incoming light while photoionization within the  $\sigma^*$  shape resonance produces molecular ions with orientation preferentially parallel to the electric vector. Subsequent Auger-decay widths<sup>4</sup> of the  $K$ -shell vacancy are typically 0.2–1 eV while rotational spacings are typically 0.001 eV, so that the orientation of the photoexcited molecule, i.e., the specific direction of the molecular axis, changes negligibly between the creation of the  $K$ -shell vacancy and its subsequent decay. Thus, the angular distributions of ionic fragments from Auger final molecular states, as a function of photoexcitation energy, should provide us with a spectroscopy of the an-

isotropy of molecular photoabsorption in a randomly oriented gas-phase target. Also, the angular distribution of a particular Auger emission can mirror the anisotropy of the molecular photoabsorption.<sup>3</sup>

From Auger-emission measurements, Truesdale *et al.*<sup>5</sup> observed that the discrete  $\pi^*$  resonance as well as the continuum  $\sigma^*$  shape resonance of CO showed nearly isotropic decay behavior. For  $N_2$ , Lindle *et al.*<sup>6</sup> observed the similar isotropic decay behavior. However, using higher-resolution Auger measurements, Becker *et al.*<sup>7</sup> found anisotropic behavior at the  $\pi^*$  resonance of CO, but no comparable effect across the  $\sigma^*$  shape resonance. In this Letter we report the first measurements of fragment-ejection asymmetries as a "direct" probe of the anisotropy of molecular photoabsorption in the vicinity of the  $\pi^*$  discrete and  $\sigma^*$  shape resonances of  $N_2$ . The kinetic energies of the ionic fragments, which provide additional important information on molecular dissociation following  $K$ -shell excitation, have been "directly" determined for the first time in the present work, in contrast to the indirect determination<sup>8</sup> of kinetic energies from an analysis of time-of-flight spectral profiles corresponding to the ionic fragments.

The angle-resolved photoion measurements were carried out with use of synchrotron radiation emitted from an undulator<sup>9</sup> inserted in the 2.5-GeV Photon Factory storage ring. The radiation was monochromatized by a 10-m grazing-incidence monochromator<sup>10</sup> with a bandwidth of 0.6 eV at  $\hbar\omega = 400$  eV. The monochromatic photon beam (approximately  $10^{11}$  photons/s) was focused onto the interaction zone in a gas cell. The density of molecules in the interaction region was estimated to be about  $10^{12}$  molecules/cm<sup>3</sup>. Photoions emerging from the interaction zone and passing through the slit of the gas cell were energy analyzed and detected by a

parallel-plate electrostatic analyzer<sup>11</sup> combined with a position-sensitive detector. Although the rotatable electrostatic analyzer was usually used for electron detection, it was a simple matter to convert it to the ion-detection mode by switching the power-supply polarities. To improve the sensitivity of ion detection, a high voltage of  $-2$  kV was applied to the input surface of a microchannel plate, and an electric-shielding thin electrode with high transmission was inserted between the inner plate of the analyzer and the microchannel plate. A large (100-eV) kinetic energy in the dispersive element was used to record an entire spectrum at a time, resulting in a nominal resolution of 0.5 eV for singly charged ions. Spectra were recorded at two angles of  $0^\circ$  and  $90^\circ$  relative to the polarization direction of the incoming light. The effective acceptance angle of the analyzer was estimated to be about  $\pm 2^\circ$ . The degree of linear polarization of the undulator radiation with a limited divergence angle of 0.066 mrad had previously been determined by measuring the angular distribution of photoelectrons from helium, and turned out to be 100% with the polarization direction parallel to the storage-ring plane.<sup>12</sup> Although six optical components reflecting the undulator radiation horizontally are installed in the 10-m grazing-incidence monochromator beam line,<sup>10</sup> it is assumed that the degree of linear polarization for monochromatized radiation remains 100%. This is reasonable because no  $p$  component of polarization is included in the primary undulator radiation with 0.066-mrad divergence.

Figure 1 shows representative photoion kinetic-energy spectra resulting from  $K$ -shell photoexcitation and photoionization of  $N_2$  by 401- and 419.3-eV photons. The zero point in the energy scale has been determined from the peak position corresponding to atomic photoions  $Kr^{n+}$ . The present spectra are not corrected for the transmission of the spectrometer, which is higher for slower particles. The lack of correction does not interfere at all with the angular dependence of these spectra. The dependence of the spectra on the angle of observation  $\theta$  relative to the polarization direction of the incoming light is seen qualitatively in the  $\theta=0^\circ$  and  $90^\circ$  spectra and will be discussed below. The identification of the spectral features is as follows: The strong peak near zero kinetic energy of Fig. 1(a) comprises mostly  $N_2^+$  ions and that of Fig. 1(b),  $N_2^{2+}$  ions.<sup>7,13</sup> These molecular ions have a thermal energy distribution. The kinetic energies of fragment ions are estimated from the energy differences between the binding energies of the initial two-hole states of  $N_2^{2+}$ , which were determined by Auger-electron spectroscopy,<sup>14</sup> and the threshold energies of specific dissociation channels. The broad channel centered at 5.6-eV kinetic energy is mainly attributable to the dissociation  $N_2^{2+}$  ( $47.4 \pm 3$  eV)  $\rightarrow$   $N^+(^3P) + N^+(^3P)$  (38.8 eV). The 5.6-eV kinetic energy for the  $N^+$  ion agrees well with that ( $5.5 \pm 0.8$  eV) determined by Eberhardt *et al.*<sup>8</sup> from time-of-flight spectra taken in

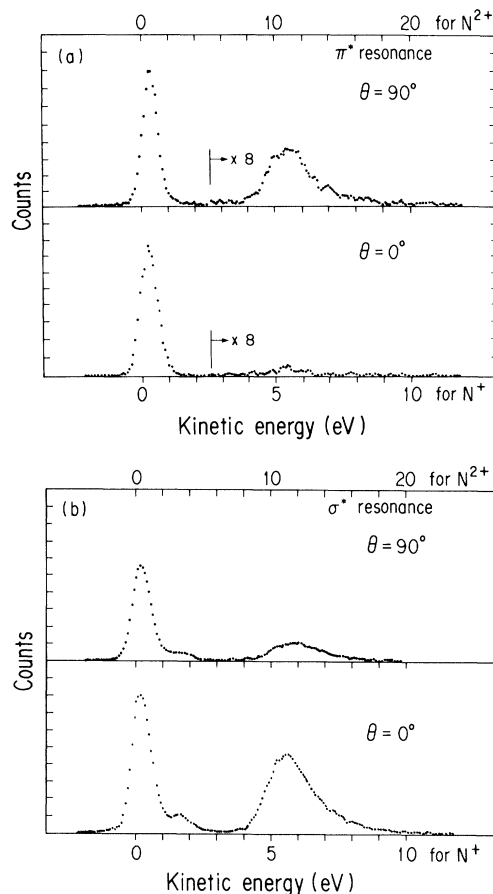


FIG. 1. Photoion kinetic-energy spectra for photoionization of  $N_2$  at (a) the  $\pi^*$  discrete resonance of 401 eV and (b) the  $\sigma^*$  shape resonance of 419.3 eV. The broad bands centered at 5.6-eV kinetic energy, for two observation angles ( $\theta=0^\circ, 90^\circ$ ) relative to the polarization direction of the incoming light, show strongly anisotropic distributions of fragment ions; at the  $\pi^*$  resonance the molecular axis is oriented perpendicularly to the polarization direction and at the  $\sigma^*$  resonance the axis is mainly oriented along that direction. Note that these spectra are uncorrected for the spectrometer transmission function. The data are processed with five-point smoothing. The uncertainty of the kinetic-energy scale is  $\pm 0.2$  eV for  $N^+$  ions.

coincidence with Auger electrons. The tail around 8 eV of the band is probably caused by the dissociation  $N_2^{2+}$  ( $\sim 60$  eV)  $\rightarrow$   $N^+ + N^+$  ( $> 38.8$  eV). It is also possible that this two-hole state of  $N_2^{2+}$  with  $\sim 60$ -eV binding energy dissociates into  $N^{2+}(^2P) + N(^4S)$  with 54-eV threshold energy. This dissociation process may be assigned to the weak band around 3 eV in the energy scale of  $N^{2+}$ . The dissociation channel  $N_2^{2+}$  (71 eV)  $\rightarrow$   $N^{2+}(^2P) + N(^4S)$  (54 eV) would produce ions with about 8.5-eV kinetic energy. The broad band centered at 5.6 eV in the energy scale of  $N^+$  encompasses the contribution of  $N^{2+}$  ions with 8.5-eV kinetic energy in the energy scale of  $N^{2+}$ . For  $N^{2+}$ , the kinetic energies

of the present measurements disagree with those determined by Eberhardt *et al.*<sup>8</sup>; in the present spectra there are no peaks around 6.7-eV kinetic energy (in the energy scale of  $N^{2+}$ ) derived by those authors, and the 3-eV kinetic energy obtained by the present measurements was not derived by them. The discrepancies may be resolved by taking the angular distribution of the fragments into account in the procedure to analyze the profiles of the time-of-flight spectra.

Now let us turn to the angular distribution of the fragments that is the main purpose of this study. For randomly oriented molecules with cylindrical symmetry in the gas phase, within the framework of the dipole approximation, it has been shown theoretically<sup>3,15,16</sup> that the molecular orientation along the direction  $\Omega_m$  is described by an orientation parameter  $\beta_m$ :

$$\frac{d\sigma(\hbar\omega)}{d\Omega_m} = \frac{\sigma(\hbar\omega)}{4\pi} [1 + \beta_m(\hbar\omega)P_2(\cos\theta_m)], \quad (1)$$

where  $\theta_m$  ( $=\theta$ ) is the angle between the molecular axis and the electric vector of linearly polarized light, and  $P_2(\cos\theta_m)$  is the second Legendre polynomial. If we introduce the photoabsorption strengths  $D_\lambda^2$  for molecular orientation along ( $\sigma$ ) or perpendicular to ( $\pi$ ) the electric vector of the light, the orientation-parameter expression is obtained theoretically<sup>16</sup> as

$$\beta_m(\hbar\omega) = \frac{2[D_\sigma^2(\hbar\omega) - D_\pi^2(\hbar\omega)]}{D_\sigma^2(\hbar\omega) + 2D_\pi^2(\hbar\omega)}. \quad (2)$$

By the application of Eq. (1) we derived the orientation parameter experimentally from the photoion spectra at  $\theta=0^\circ$  and  $90^\circ$ . Here we reasonably assumed that the molecular orientation induced by the  $K$ -shell photoabsorption holds during the subsequent Auger decay leading to the fragment ions; the axial-recoil approximation<sup>15,16</sup> is applied. Figure 2 shows the results of this study for the discrete  $\pi^*$  and continuum  $\sigma^*$  resonance regions: the total cross sections and the molecular orientation parameters obtained from the angular distributions of fragment ions corresponding to the broad band centered at the 5.6-eV kinetic energy. We see that the orientation parameters drop sharply to  $\beta_m = -1$  at the  $\pi^*$  discrete resonance position, as expected theoretically from Eq. (2), and show significant variation across the  $\sigma^*$  shape resonance, that is, the strong resonance enhancement of the  $D_\sigma^2$  component compared with the almost constant  $D_\pi^2$  in Eq. (2). In contrast to the present results, the Auger-emission measurements showed nearly isotropic decay behavior across the  $\sigma^*$  shape resonance.<sup>5-7</sup> The angular distribution of the Auger electrons is indirectly connected with  $\beta_m$ ; the Auger asymmetry parameter  $\beta_e$  can be written as  $\beta_e = C_e\beta_m$ ,<sup>3</sup> where  $C_e$  is a constant characteristic of each Auger-decay channel. Although Dill *et al.*<sup>3</sup> expect that  $C_e$  is nonzero in general because of the highly anisotropic charge distributions of molecules with  $K$ -shell vacancy, the experi-

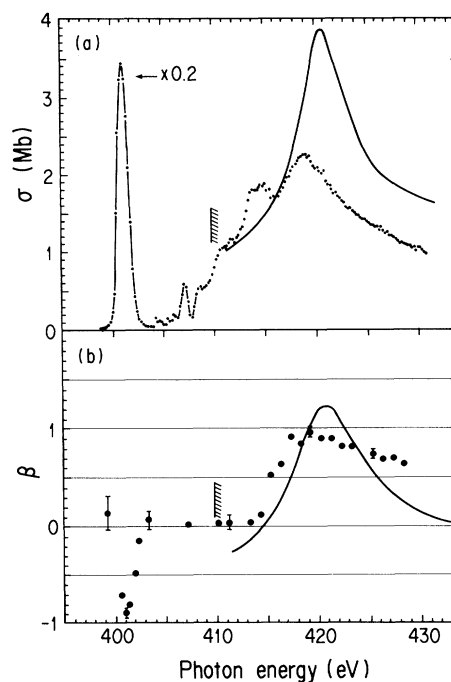


FIG. 2. (a) Total photoionization cross sections and (b) molecular orientation parameters in the vicinity of the  $\pi^*$  and  $\sigma^*$  resonances of  $N_2$ . To measure the cross sections, photoions passing through the slit of the gas cell are detected by a micro-channel plate without any energy selection. The data are normalized to the absolute value of Bianconi *et al.* (Ref. 17) at the  $\sigma^*$  resonance peak of 419 eV. The solid curve in (a) is the theoretical prediction by Dill *et al.* (Ref. 18). The orientation parameters are obtained from the angular distributions of the broad bands, from 3.5 to 8.9 eV, centered at 5.6 eV in the kinetic-energy spectra. The error bars represent the differences of background subtraction only. The solid curve in (b) is the theoretical calculation by Dill *et al.* (Ref. 3).

mental results<sup>5-7</sup> showed the  $C_e$  to be very close to zero as mentioned in the introduction. In the present fragment-ion measurements, we can determine the molecular orientation "directly," because the molecular axis changes negligibly in the course of the decay. It should be emphasized that the fragment measurements are excellent as a probe of the molecular orientation induced by the  $K$ -shell photoabsorption and that Auger measurements may be unsuited. The behavior of the orientation parameters across the  $\sigma^*$  continuum shape resonance agrees qualitatively with that calculated by Dill *et al.*<sup>3</sup> That is, the orientation along the electric vector is considerable in both cases. Total photoionization cross sections across the  $\sigma^*$  shape resonance exhibit qualitative agreement with those calculated by Dill *et al.*<sup>18</sup> From the agreements on the orientation parameters and photoionization cross sections, we can conclude that the multiple-scattering method, which was employed in the calculation of Dill *et al.*,<sup>3,18</sup> is a good model for the con-

tinuum shape resonance.

In summary, we have observed for the first time fragment-ejection asymmetries arising from anisotropic *K*-shell photoexcitation of a free molecule. Because the molecular orientation induced by the excitation process is "directly" reflected in the ejection angle of fragments, the present technique, i.e., angle-resolved photoion spectroscopy, has been used as a "direct" probe of the symmetry of a photoexcited molecule. As a result, the present data confirmed nicely the prediction made by Dill *et al.*<sup>3</sup> The present technique will be applicable to the "direct" determination of the orientation of molecules chemisorbed on surfaces.

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