Auger-Electron–Ion Coincidence Studies of Soft X-Ray–Induced Fragmentation of N_2

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We report a coincidence experiment between energy-selected Auger electrons and the ions produced in the molecular fragmentation following core photoionization of N_2. In this type of measurement it is possible to correlate the ion fragmentation products, their kinetic energy, and their electronic configuration with the hole configuration in the doubly charged molecule following the Auger decay of the initial core hole. These data produce new insight into the potential-energy curves of the doubly charged molecular ions.

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Absorption of a soft x-ray photon creating a core hole in an isolated molecule leads to a chain of events, the end result of which is usually the production of ionic fragments of the parent molecule. The initial photoabsorption process leaves the molecule (or molecular ion) in a highly excited state, which decays filling the core hole either by Auger decay or by fluorescent decay. For a low-Z atom like nitrogen the Auger decay dominates. This molecular ion formed by the Auger decay of the core hole can fragment into various products depending upon the specific valence-hole configuration. We report in this Letter the first coincidence measurements between the energy-resolved Auger electrons and the ion fragments. These measurements can identify the fragmentation products associated with a given valence-hole configuration.

The general experimental arrangement has been described previously.[1] The electrons are detected by a cylindrical mirror analyzer (CMA) while the ions are detected by a time-of-flight (TOF) mass spectrometer, 180° from the axis of the CMA and perpendicular to the light beam. Every pulse recorded by the CMA, set to detect electrons of a specific energy, starts the time to digital converter which is stopped by pulses coming from the TOF. The major experimental difficulty in any coincidence experiment is to differentiate between true and accidental coincidences. This is made more severe by a synchrotron source which is pulsed, since the accidental coincidences carry the time structure of the source. The curves shown in this Letter have had the machine time structure removed by using a portion of the spectrum containing only accidental coincidences.[1]

The quasimonochromatic radiation of energy 1200 eV produced by the 36-pole undulator was used to ionize a beam of N_2 molecules.[1] A large fraction of the energy of the absorbed photon is carried away by the ejected electron with the molecular ion retaining by definition the binding energy (E_B) of a N_{1S} electron in N_2 ($E_B=409.9$ eV[2]). The N_{1S} core hole decays by an Auger process leaving two holes in the valence levels. The binding energy of this two-hole state can be determined by measuring the kinetic energy of the peaks in the Auger spectrum, and subtracting this energy from the N_{1S} binding energy. Figure 1(a) displays our Auger spectrum for N_2 plotted on this binding-energy scale.[3-5]

The energy thresholds for any specific fragment can be predicted by use of an adiabatic energy cycle. The first step is to add the energy necessary to dissociate the molecule; then each atom is ionized to a specific charge state by the addition of the appropriate energy.[6] The energy calculated by use of this procedure is the minimum energy that must be added to the molecule to produce the designated ionic products. These threshold energies[7] are plotted in Fig. 1(b), below the Auger spectrum of N_2 shown in Fig. 1(a). Notice that the threshold energy for the production of N^++N^+ is 38.8 eV. Therefore, the lowest energy state of ${N_2}^{2+}$ populated by the Auger decay (peak No. 1 at $E_B=43.2$ eV) is metastable and possibly can fragment into $N^+(^3P)+N^+(^3P)$ with ∼2 eV kinetic energy per N ion. The relationship between the binding energy of the initial two-hole state of ${N_2}^{2+}$, the fragmentation products, and their kinetic energy can be

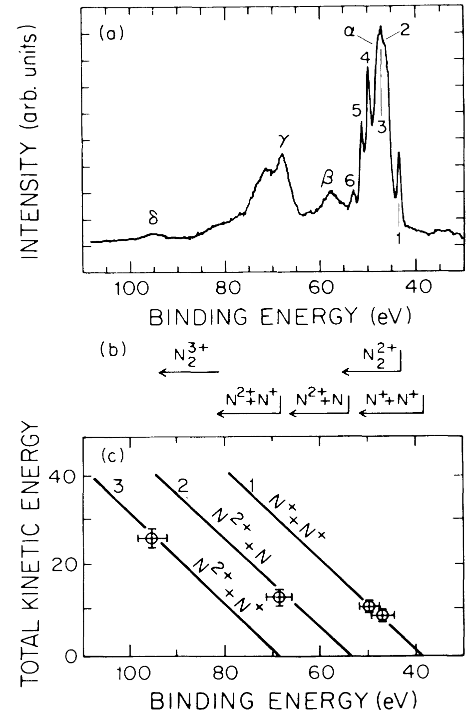

FIG. 1. (a) The N_{1S} Auger spectrum of N_2, plotted as a function of the two-hole binding energy; (b) a plot of the energy thresholds for formation of various ion fragments or multiply charged states of N_2; (c) a plot of the total kinetic energy of the fragmentation products as a function of the binding energy.

displayed by use of Fig. 1(c). In this figure the total kinetic energy of the fragmentation products is plotted against the Auger-electron binding energy. Each one of the diagonal lines represents a specific fragmentation product, i.e., line 1 is for the $N^+ + N^+$ product with both ions in the ^3P ground state. There should be other lines in Fig. 1(c) for the dissociation of N^{2+} into excited states of N^+ (the ^1S state is ∼4 eV higher in energy than the ^3P). Fragmentation may not occur in the time scale of our measurement because of a large potential barrier for dissociation.[8] The Auger-electron–ion coincidence measurements reported in this Letter will be used to determine the qualitative shape of the potential energy curves and the fragmentation products as well as the excited-state configuration of these products as a function of the electronic configuration of the molecule before fragmentation.

Figure 2 shows a series of Auger-electron–ion coincidence spectra for N_2. The high-resolution TOF mass/charge spectra for the region of N^{2+} ($m/e = 7$) is shown on the left and the $m/e = 14$ region is presented on the right. These were the only regions in the TOF spectra where we had a signal. When a fragment like N^+ has kinetic energy the TOF spectra will exhibit two peaks; the shorter time peak is produced by those ions that were originally headed away from the detector but are turned around by the extraction field.[1] The kinetic energy of the fragmentation products can be determined from the time-of-flight spectra by use of computer simulation of the ion trajectories in the spectrometer. The letter (A–F) associated with each set of TOF spectra is used to label the energy position in the Auger spectrum at the top left of Fig. 2. The Auger spectrum at the top right is like the one shown in Fig. 1(a), taken with no extraction voltage in the TOF. In order to increase the ion collection efficiency in the TOF an extraction voltage must be used which degrades the electron resolution, producing the type of Auger spectrum at the top left.[1]

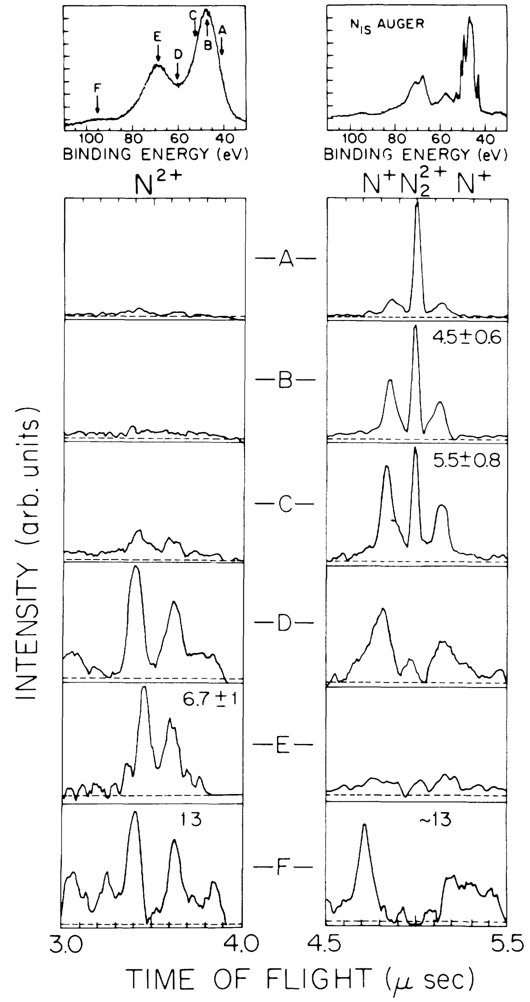

FIG. 2. TOF ion mass spectra of N_2 taken in coincidence with the Auger electrons at the various kinetic energies indicated by the arrows A through F. The kinetic energy of the fragments (electron volts) is indicated above the strongest peaks.

Now let us examine the details of the TOF mass spectra as a function of the binding energy of the Auger electron (or hole configuration). The TOF spectra marked A were accumulated for a binding energy of 43 eV, corresponding to the highest energy peak in the Auger spectrum [marked 1 in Fig. 1(a)]. There is some disagreement in the literature concerning the assignment of this peak,[3,4,8,9] with the two possibilities being the $^3\Pi_u[3\sigma_g^{-1},1\pi_u^{-1}]$ or the $^1\Sigma_g^+[3\sigma_g^{-2}]$ states of $N_2{}^{2+}$. Our data show that the primary product at point A is either $N_2{}^{2+}$ or N^+ with no kinetic energy. It is impossible to have $N_2{}^{2+}$ decay into $N^+ + N^+$ with no kinetic energy because of the Coulomb explosion between these two positively charged ions. Therefore, our data in conjunction with the high-resolution Auger data[5] prove that the majority of the intensity in this peak comes from a state of $N_2{}^{2+}$ that is trapped in a virtual bound state with its minimum at approximately the same interatomic spacing as N_2. This is the $^1\Sigma_g^+[3\sigma_g^{-2}]$ state which according to theory has a 2.4-eV potential barrier for dissociation.[8] The weak peaks in the TOF spectra A on either side of the main $N_2{}^{2+}$ peak are produced by N ions with ~ 4.5 eV kinetic energy. They are most likely a consequence of the poor electron resolution picking up contributions from other hole configurations. The metastable $N_2{}^{2+}$ ions must live long enough to escape from the extraction region into the drift tube (~ 1 μsec). If the molecular ion fragments in the drift tube the TOF spectrometer will not measure the kinetic energy because the m/e ratio stays the same and the kinetic energy is small compared to the acceleration voltage.

Point B in the Auger spectra is the region of the most intense emission ($E_B \sim 47$ eV), and according to the calculation by Agren[3] the majority of the intensity comes from the following configurations: 43% from the $^1\Delta_g[1\pi_u^{-2}]$, 25% from the $^1\Sigma_g^+[1\pi^{-2}]$, and 24% from the $^1\Pi_u[3\sigma_g^{-1},1\pi_u^{-1}]$. The calculated potential-energy curve for the $^1\Delta_g$ state is repulsive while the $^1\Pi_u$ and $^1\Sigma_g^+$ states exhibit a potential minimum for $N_2{}^{2+}$.[8] This theoretically derived picture is in qualitative agreement with the experimental observation displayed in panel B of Fig. 2. The central peak in the TOF spectrum is from $N_2{}^{2+}$ while the two broad peaks on either side are caused by N^+ with 4.5 ± 0.6 eV kinetic energy. This kinetic energy is plotted on Fig. 1(c) showing that it is consistent with fragmentation into $N^+ + N^+$ in the ^3P state.

Panel C shows the coincidence spectra taken at a binding energy of ~ 50 eV, which averages over the peaks labeled 4 and 5 in Fig. 1(a). At this point in the Auger spectrum the only fragmentation products are $N_2{}^{2+}$ and N^+ (with 5.5 ± 0.8 eV kinetic energy). There is a small contribution of N^{2+} signal seen in the left-hand panel of C which again is a consequence of our poor electron energy resolution picking up signal from deep enough in the Auger spectrum to be above the threshold for formation of $N^{2+} + N$ (54 eV). Peak No. 4 in the Auger spectrum is assigned to the $^1\Pi_g[2\sigma_u^{-1},1\pi_u^{-1}]$ state of $N_2{}^{2+}$ and according to theoretical calculations the potential-energy curve for this state is repulsive.[8] In contrast, peak No. 5 has been assigned to the $^1\Sigma_u[2\sigma_u^{-1},3\sigma_g^{-1}]$ state of $N_2{}^{2+}$ which exhibits a potential curve with a metastable bound state for $N_2{}^{2+}$. The experimental data at point C are consistent with this picture. The $^1\Pi_g$ state has a binding energy of 49.5 eV (Ref. 5) so that fragmentation into $2N^+(^3P)$ would produce ions with 5.4 eV kinetic energy while we measure 5.5 ± 0.8 eV. The observation of a $N_2{}^{2+}$ signal in panel C indicates that the $^1\Sigma_u$ state of $N_2{}^{2+}$ is indeed temporarily trapped in a virtual bound state. At point D ($E_B \sim 60$ eV) in the Auger spectrum a significant contribution from N^{2+} is present in the TOF spectra, because the binding energy is above the threshold for formation of $N^{2+} + N$. The low intensity of the peaks in this region of the spectrum [β region of Fig. 1(a)] coupled with our poor energy resolution makes any quantitative assignment of the configuration of the fragmentation products from our data very suspect.

At point E in the Auger spectrum the decay of the hole states marked by the γ in Fig. 1(a) are measured. These states correspond to one hole in the $2\sigma_g$ and a second hole in an outer valence state, i.e., $2\sigma_u$, $1\pi_u$, or $3\sigma_g$. It is amazing that the only observed decay channel is $N_2{}^{2+} \rightarrow N^{2+} + N$. Conservation of momentum allows the energy of the neutral N to be determined and therefore the total kinetic is (13.4 ± 2.0 eV). Argen[3] has shown theoretically that the γ region of the N_2 Auger spectrum is composed of three main peaks associated with the $^1\Sigma_g[2\sigma_g^{-1},3\sigma_g^{-1}]$ state at 67 eV, the $^1\Sigma_u[2\sigma_g^{-1},3\sigma_u^{-1}]$ state at 71 eV, and the $^1\Pi_u[2\sigma_g^{-1},1\pi^{-1}]$ state at 73 eV. The measured kinetic energy is sufficient to allow the $^1\Sigma_g$ state to decay into the ground state of $(^2P^\circ) + N(^4S^\circ)$, but the kinetic energy is too small, even within the appreciable experimental uncertainty, for the $^1\Sigma_u$ and $^1\Pi_u$ states. The explanation is quite obvious. These singlet states of $N_2{}^{2+}$ cannot fragment into a doublet plus a quartet.[10] There are three decay channels in approximately the correct energy range with the correct electronic and multiplet structure: $N^{2+}(^2P^\circ) + N(^2D^\circ)$ with a threshold energy of 56.3 eV, $N^{2+}(^2P^\circ) + N(^2P^\circ)$ with a threshold energy of 57.4 eV, and $N^{+2}(^4P) + N(^4S^\circ)$ at 61 eV. The last two channels are slightly more favored by the experimental data than the first possibility.

Region δ of the Auger spectrum in Fig. 1(a) and marked by F in Fig. 2 corresponds to two holes in the $2\sigma_g$ orbital.[3] It is now energetically possible to form $N_2{}^{3+}$, but this triply charged species cannot be formed by a second Auger decay of the states at δ. There is too much energy stored in the remaining $2\sigma_g$ hole, so only shake off in the first Auger process can form $N_2{}^{3+}$. The sum of the kinetic energies for N^{2+} and N^+ observed at F is plotted in Fig. 1(c), which shows that it is consistent with the fragmentation of $N_2{}^{3+} \rightarrow N^{2+} + N^+$.

Our data for the fragmentation of $N_2{}^{2+}$ can be combined with the theoretical calculations of Thulstrup and

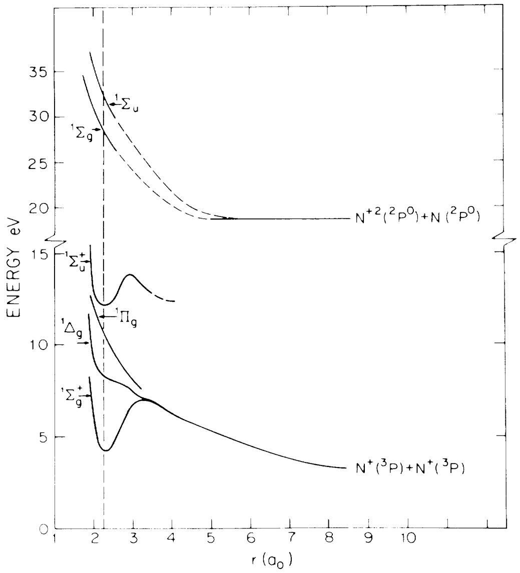

FIG. 3. Potential-energy curves for selected states of $N_2{}^{2+}$ created by combining the experimental data presented in this paper with the theoretical calculations of Thulstrup and Andersen (Ref. 8).

Andersen[8] to create a partial set of potential-energy curves for different molecular ion states of $N_2{}^{2+}$. Figure 3 displays these potential-energy curves. At present we know the excitation energy at the spacing of N_2, the energy and configuration of the fragmentation products at large separation, the shape of the Coulomb repulsive curve at large separation for two charged particles, and which states have a virtual bound state. Combining high-resolution Auger spectra with our data will enable the experimentalist to determine the shape and relative position of the virtual bound potential wells.

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