Correlation between Electron Emission and Fragmentation into Ions following Soft-X-Ray Excitation of the N_2 Molecule

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The authors present the first simultaneous studies of fragment ion production and electron emission of a molecule following deep core-level excitation. Using synchrotron radiation they tune in to various absorption resonances and correlate certain electron-hole states in the decay of the x-ray excitation with the appearance of specific ionic fragments. For N_2 specifically they observe a 1:1 correspondence between single valence hole states and undissociated N_2^+ after N $1s \rightarrow \pi^*$ excitation and relate the production of N^{++} ions to the generation of holes in the $2\sigma_u$ orbital.

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Soft-x-ray absorption in a molecule involving excitation of a core electron into an unoccupied molecular orbital, into a Rydberg state, or into the continuum usually results in a fragmentation of the molecule.[1-4] The initial excitation is followed by an Auger-type transition which depletes the bonding orbitals and partially occupies antibonding orbitals such that the molecule falls apart into various ionic fragments. The ions observed may have considerable energy if both fragments are ionic which had led to the term of "Coulomb explosion" of the molecule.[1] Here we report for the first time simultaneous studies of the ionic fragmentation and electron emission of N_2 at photon energies around the N 1s absorption threshold using synchrotron radiation. Thus we are able to correlate the electronic states after the deexcitation of the N 1s core hole with the observation of ionic fragments. In general we find that single-electron emission from outer valence levels produces N_2^+ ions, whereas two holes in the valence shell or a hole and an electron-hole pair, a shakeup configuration, lead to ionic fragments.

The experiments were performed at the Stanford Synchrotron Radiation Laboratory on the new grasshopper beam line.[5] The experimental setup is described elsewhere[6] and includes an ion chamber for absorption measurements, a time-of-flight (TOF) mass spectrometer, and a commercial PHI 15-255 G double-pass cylindrical-mirror electron energy analyzer (CMA). Vacuum separation from the ultrahigh-vacuum beam line is achieved via a double-stage differential pumping system and a metallic capillary array having an optical transmission of about 50%. This differential pumping arrangement gives a pressure differential of six orders of magnitude between the experimental chamber, which typically operates at 10^{-4} Torr, and the beam line.

Figure 1 shows the total electron yield, the total ion yield, and the production of possible singly and doubly charged ionic species as functions of photon energy around the N 1s absorption threshold. The total ion yield is given by the integrated counts in the TOF mass spectrometer. The e^- yield is measured with a Channeltron opposite the TOF detector. In order to take the fragment-ion curves we delay the electron pulse indicating an absorption event by the flight time of a specific ion fragment and check for coincidence with the TOF ion signal. Typical flight times were about 2.5 μsec for N^+. The performance of the TOF mass spectrometer is described elsewhere.[6]

The strong absorption peak at 401 eV is due to

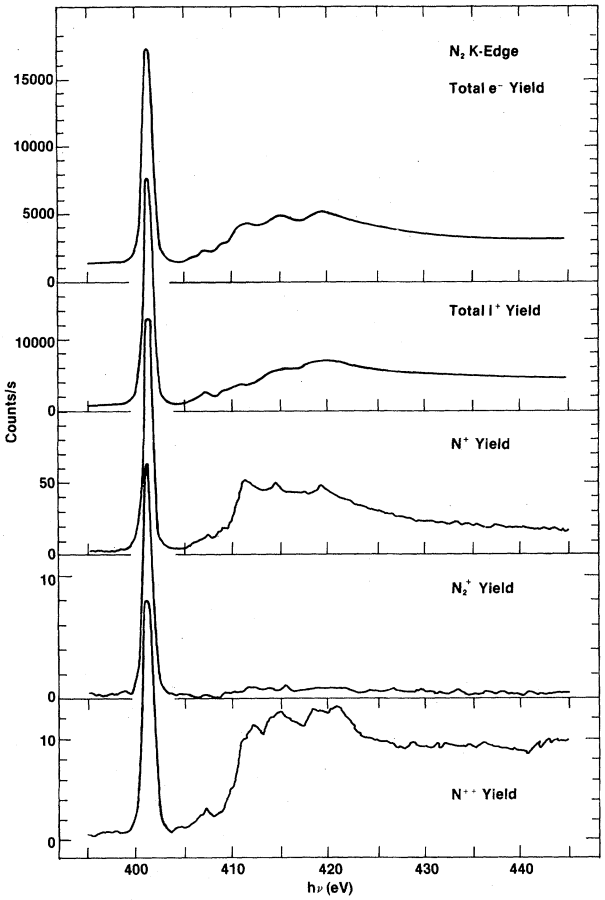

FIG. 1. Total electron, total ion, and mass-specific ion yields at the onset of the N 1s absorption. The N 1s ionization threshold is indicated at 409.9 eV (Ref. 6). The normalized counting rates are shown in counts per second for each individual channel. Because of the coincidence technique described in the text, the mass-specific ion yields do not add up to the total ion yield.

transitions from the N 1s core level into the unoccupied $1\pi_g$ molecular orbital. The width of this π^* resonance is limited in our results by the monochromator resolution. The absorption structures between 401 and 415 eV have all been observed previously and assigned to various discrete excitations of the N 1s electron.[7,8] This includes transition into Rydberg-type orbitals, the continuum threshold, and thresholds for shakeup excitations. The peak at 418 eV is due to a final-state continuum shape resonance of σ_u symmetry[5,6] rather than a bound-state excitation. The N 1s ionization threshold is indicated at 409.9 eV.[6] Threshold and low-kinetic-energy electrons are collected by the Channeltron with a larger phase-space acceptance than Auger electrons. Therefore the part of the electron spectrum above the ionization continuum appears slightly enhanced in intensity compared to an absorption spectrum.[7,8] This is not the case for the ion yield because the accelerating field essentially collects all ions generated at the crossing between the ion beam and the photon beam.

TABLE I. Branching ratios of ionic fragments of N_2 (in percent).

$h\nu$ (eV)	N^+ [a]	N_2^+	N^{++}
401	79	9.5	11.5
407.5	87.5	0	12.5
412	83	~ 0.5	16.5
418	78.5	~ 0.5	21
440	65	0	35

[a]According to Ref. 1 the N_2^{++} is less than 5% of the N^+ yield after N 1s ionization.

Comparing the mass-resolved ion-yield curves in Fig. 1, we make two general observations: (i) N_2^+ is found essentially only at the π^* resonance and (ii) the branching ratio between N^{++} and N^+ changes by a factor of 2 in favor of N^{++} above the onset of continuum absorption. The measured ion branching ratios are given in more detail in Table I for photon energies corresponding to various excitations of the N 1s electron. Since the total valence-electron absorption amounts to less than 1.5% of the cross section of the π^* resonance, as measured earlier[8] and verified by the low N_2^+ yield for photon energies less than 401 eV, we have decided to omit in our following discussion any processes involving direct photoionization of the valence levels ($2\sigma_g$, $2\sigma_u$, $1\pi_u$, $3\sigma_g$) and rather to concentrate on the N 1s excitations. The 14-u peak obviously represents both species, N^+ and N_2^{++}. However, previous studies of N_2 and isotopes of O_2 with x-ray line sources suggest that N^+ is the predominant ($\gtrsim$ 95%) species in the 14-u peak.

In order to understand the changes in the fragmentation pattern for the various excited states of the N 1s electron we have studied the electronic decay of the N 1s hole after either π^* or continuum excitation. This has led to the choice of 401- and 418-eV photon energy in our examples. Since nitrogen is a light element the 1s hole decays predominantly via an Auger-type transition. This process is faster than the fragmentation. Therefore the energy spectrum of the emitted electrons allows us to deduce the relative popu-

lation of various single-hole, two-hole, or two-hole, one-electron states of the molecule prior to its breaking into ionic fragments. These electron emission spectra are shown in Fig. 2. The top spectrum is taken under white x-ray irradiation containing all photon energies as transmitted in zero order of the monochromator. This spectrum is virtually identical to the previously known Auger spectrum of N_2 generated by electron bombardment.[9,10] Comparing x-ray and electron excited spectra, Moddeman *et al.*[10] concluded that the "typical" electron-excited N_2 Auger spectrum also contains lines generated in the decay of bound-state transitions, like N $1s \rightarrow \pi^*$, and does not exclusively show the decay of the N 1*s* ionized core hole. The π^* excitation decays in an autoionizing process in the neutral molecule and therefore will produce electrons of higher kinetic energies than the normal Auger transition. This effect is illustrated in the lower two curves in Fig. 2. The center spectrum shows the "pure" Auger spectrum generated in the decay of a completely ionized N 1*s* core hole whereas the bottom spectrum shows the electrons emitted following

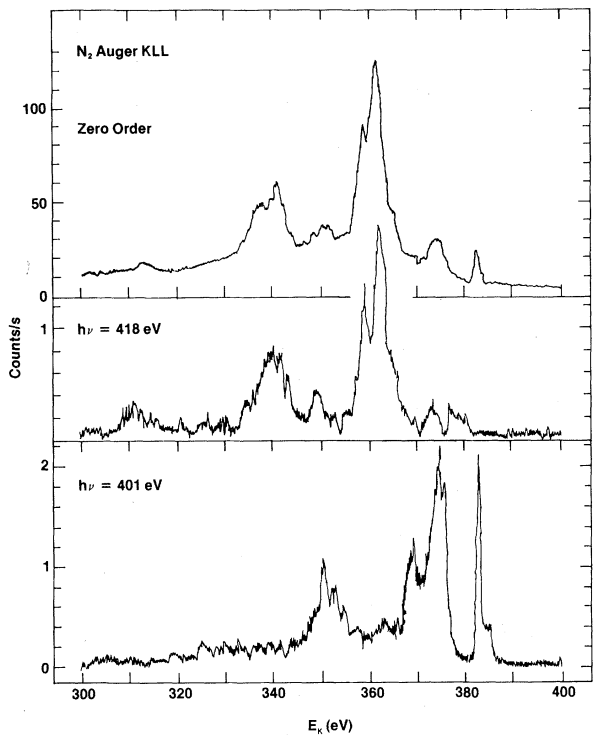

FIG. 2. Electron energy distribution curves after excitation with white light (top) and monochromatic light of 418-eV (middle) and 401-eV (bottom) energy. The peaks are assigned to various electron-hole configurations in the text.

the decay of the π^* resonance. This process was also studied with use of an $(e,2e)$ coincidence technique, but only the high-energy decay processes (above $E_k = 360$ eV) were shown.[11]

The peaks in the Auger spectrum taken with 418-eV photons can be assigned to various two-hole and possible three-hole states of N_2 as for the Auger spectra reported earlier.[9,10] In general the lines between 355 and 370 eV correspond to two-hole states where both holes are located in the outer valence orbitals ($2\sigma_u$, $1\pi_u$, $3\sigma_g$). The peak around 340 eV corresponds to one $2\sigma_g$ hole together with an outer valence hole and the peak at 312 eV has been assigned to the $(2\sigma_g)^{-2}$ $1\Sigma_g^+$ state.[9,10] The similarity of our spectrum shown here compared to an x-ray–excited N_2 Auger spectrum[10] demonstrates that the electron is not trapped long enough in the shape resonance to have a significant influence on the Auger decay of the N 1*s* hole.

The assignment of the bottom spectrum of Fig. 2 is almost as straightforward. The decay of the π^* resonance may occur in two possible ways. One involves the electron in the $1\pi_g$ orbital and essentially ends up in a single-hole state just like in a single-particle photoemission process. Energy conservation tells us that the lines around 385 eV correspond to processes of this type and in particular the strong line at 383 eV (385 eV) corresponds to a $1\pi_u$ ($3\sigma_g$) hole. The second process essentially leaves the $1\pi_g$ electron as a spectator and creates two additional valence holes. These states correspond to shakeup states observed in valence photoemission with an electron excited into the $1\pi_g$ orbital. In these valence photoemission shakeup states the strongest lines correspond to a $1\pi_u \rightarrow 1\pi_g$ shakeup transition.[12-14] Pursuing this new, but probably oversimplified, approach, we come to the following peak assignments: The peaks at 375 and 369 eV correspond to a $3\sigma_g^{-1}1\pi_u^{-1}1\pi_g$ state, the peak at 363 eV corresponds to the $2\sigma_g^{-1}$ single-hole configuration, and the peak at 351 eV is assigned to $2\sigma_g^{-1}1\pi_u^{-1}1\pi_g$.

In order to make a connection between these electronic states of the N_2 molecules and the observation of ionic fragments we refer to previous fragmentation studies in the valence excitation region where it was observed that outer valence ($2\sigma_u$, $1\pi_u$, $3\sigma_g$) single-electron ionization without shakeup does not lead to fragments.[15] At the N 1*s* π^* resonance we find 9.5% N_2^+ ions. The peaks at 383 and 385 eV correspond to 9.3% of the total area of the electron emission curve. Together

with the fact that at these photon energies the direct valence ionization has a negligible cross section, compared to the core excitations we are dealing with here, we can conclude that all other electron-hole configurations observed in the decay of the π^* resonance excitation lead to the production of ionic fragments. Moreover, since single outer valence-hole configurations are not observed after N 1s ionization (418 eV), we also do not expect to see any N_2^+ ions in accordance with our observation above.

Comparing the outer valence-hole configurations, the peaks between 355 (365) eV and 368 (379) eV in the center (bottom) part of Fig. 2, we find that the relative weight has shifted in favor of configurations containing $2\sigma_u$ holes. Especially the two strong peaks at 360 and 363 eV have been assigned to $2\sigma_u^{-1}3\sigma_g^{-1}$ and $2\sigma_u^{-1}1\pi_u^{-1}$ hole configurations coupled in various ways by the spin-orbit interaction.[9] If we try to correlate the observed hole configurations with the measured increase in the branching ratio of N^{++} ions above the N 1s ionization threshold, we come to the conclusion that the creation of a hole in the $2\sigma_u$ orbital seems to be leading to the production of N^{++} ions. Clearly, this statement should be verified by coincidence measurements and theoretical calculations. We also have to point out here that the $2\sigma_u$ hole configurations are certainly not the only configurations leading to N^{++} because we observe this ionic species also at the π^* resonance. Presumably another channel for the generation of N^{++} is via an Auger cascade with an intermediate hole in the $2\sigma_g$ level. However, the relative intensity of $2\sigma_g$ hole states in the electron spectrum does not change significantly between the π^* resonance and N 1s ionization whereas the N^{++} branching ratio changes by a factor of 2. Therefore we have to look for an additional channel generating this ionic species which we presumably have found in the $2\sigma_u$ hole configurations.

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