

Femtosecond Dynamics of Multielectron Dissociative Ionization by Use of Picosecond Laser

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The multiple ionization of molecular nitrogen has been studied by use of an intense picosecond laser (0.6 ps; 3×10^{15} W/cm²; wavelength 600 nm). By measurement of the energies of the various fragment atomic ions (N⁺, N²⁺, and N³⁺) with a time-of-flight mass spectrometer it has proved possible to investigate the dynamics of the multielectron dissociative ionization process on a time scale of about 30 fs.

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We wish to report preliminary results of an experiment on the multiphoton ionization of molecular nitrogen. However, we do not wish to emphasize the multiphoton aspect of the multiple ionization processes observed,¹ but prefer to describe the laser in terms of a classical electromagnetic field. The mechanism involved is thought to be similar to that invoked in order to explain the field ionization of Rydberg atoms,² but in this case the laser field is so intense that it produces a potential difference along the molecular axis comparable with the binding energy of the outer electrons in the ground state.

The idea behind the experiment is quite straightforward. A diatomic molecule is subjected to a large electric field created by a focused picosecond laser. As the molecule is ionized beyond the single-ion stage, the fragment atomic ions mutually repel in the Coulomb field and the resulting energetic ions are detected by a time-of-flight (TOF) mass spectrometer. If additional electrons are stripped away as the molecule dissociates, the ions are now subjected to an even larger Coulomb repulsion. They will gain more energy and this will be reflected in the TOF spectrum. Thus, the detailed dynamics of multielectron dissociative ionization (MEDI) can be investigated on a time scale of *femtoseconds* (the dissociation time scale), even though the laser pulse itself is of picosecond duration.

The basic components of the experiment were the following. A dye laser was pumped by a mode-locked, frequency-doubled neodymium-doped yttrium-aluminum-garnet laser, producing 2.5-ps pulses (0.6-ps pulses with a saturable absorber in the dye). These individual pulses were amplified in a dye amplifier driven by a *Q*-switched frequency-doubled neodymium-doped yttrium-aluminum-garnet laser operating at 10 Hz. The laser light was focused down to a diffraction-limited spot by an *f*/3 doublet lens corrected for spherical aberration and housed within the experimental chamber (base pressure 2×10^{-8} Torr). An identical doublet lens at the

output was used to monitor the laser characteristics. The energy reaching the focal region at a wavelength of 600 nm with use of a pulse length (FWHM) of 0.6 ps was 50 μ J per pulse, with pulse-to-pulse variations of $\pm 20\%$. Approximating the pulse shape by a *sech*² function and taking into account that 70% of the energy was contained within the Airy disk of measured diameter 4.4 μ m (theoretical maximum 84%) leads to a peak power density of 3×10^{15} W/cm².

The gas was introduced into the experimental chamber by use of a simple gas jet, giving a pressure in the focal region of approximately 10^{-5} Torr. The resulting photoions were subjected to a field in the region of 10 kV m⁻¹ and traversed a drift tube of length 50 mm. The ions passed through two concave meshes with radii of curvature equal to their distances from the interaction region and were finally detected by a pair of 35-mm-diam microchannel plates. The ion signal was fed via a preamplifier to a LeCroy model 9400 Transient Digitizer with a 100-MHz sampling frequency. Low-noise spectra such as those shown in Figs. 1 and 2 were obtained in less than 10 min with use of a 0.6-ps laser pulse width. Small shifts (≤ 50 meV) in the TOF peaks due to space-charge effects were reduced to insignificant levels by the running of the experiment at low pressures. Detector ringing was a problem that could not easily be removed [see in Fig. 2(b)]. The widths of the peaks in the TOF spectra for energetic N^{*n*+} ions mainly reflect the real kinetic-energy distributions. There is, however, a minor contribution associated with the thermal velocity distribution of the isotropically scattered component of the gas sample. The extent of the contribution, which varies with charge state and TOF, can be seen for ions with no kinetic-energy release, such as O₂²⁺ and Ar⁺.

The spectra obtained when air was introduced into the laser-focus region are shown in Figs. 1 and 2. The mass and energy resolution is high because of the small size of the focal point. Those ions which have kinetic energies above thermal can be grouped into two categories.

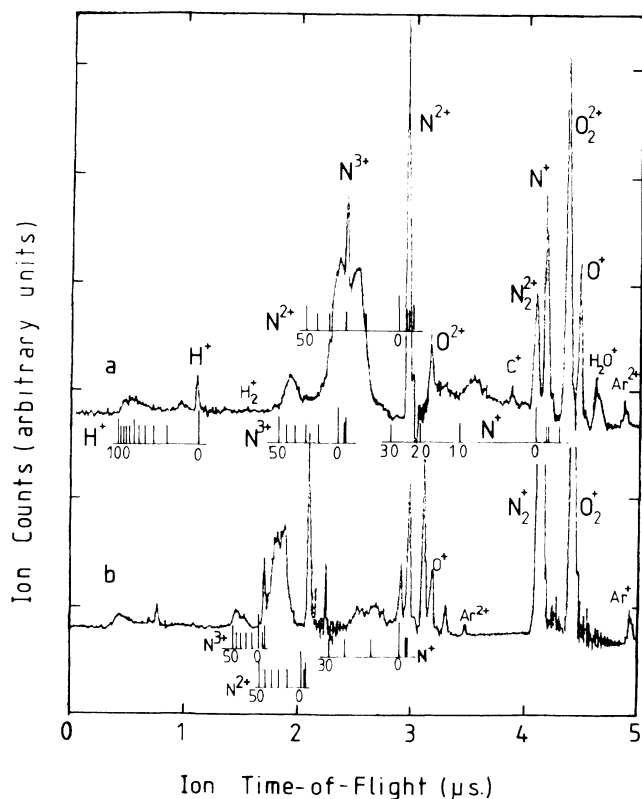


FIG. 1. The time-of-flight spectrum of air, showing the various singly and multiply charged atoms and molecules of nitrogen. The scales alongside are the kinetic-energy releases in electronvolts associated with the N^+ , N^{2+} , and N^{3+} ions. The structure associated with the energetic protons is discussed briefly in the text. (a) 50 V and (b) 100 V across the 12-mm interaction region.

Those that are initially ejected *towards* the detector have TOF's that decrease almost linearly with their initial velocity but those ejected *away* from the detector with the same velocity range virtually simultaneously at the detector. This focusing effect can be seen for the N^{2+} ions of Fig. 1(a) occurring at TOF's between 2 and 3 μ s. Ions with an energy-release spread of 10–30 eV have a range of TOF's of 0.3 μ s, whereas those ions moving away from the detector and with an identical energy-release spread arrive within a time interval of less than 0.05 μ s. The kinetic-energy release scales beneath the TOF spectra confirm this focusing effect which produces the sharp peaks for energetic ions N^+ , N^{2+} , and N^{3+} seen in Figs. 1 and 2. These energy-release scales were obtained for on-axis ions by computer simulation using a finite-difference relaxation method to determine the relevant potential distributions in the axially symmetric configuration existing here. They are valid also for forward-going, off-axis ions, because the concave meshes in front of the detector ensure the same times of flight for all ions.

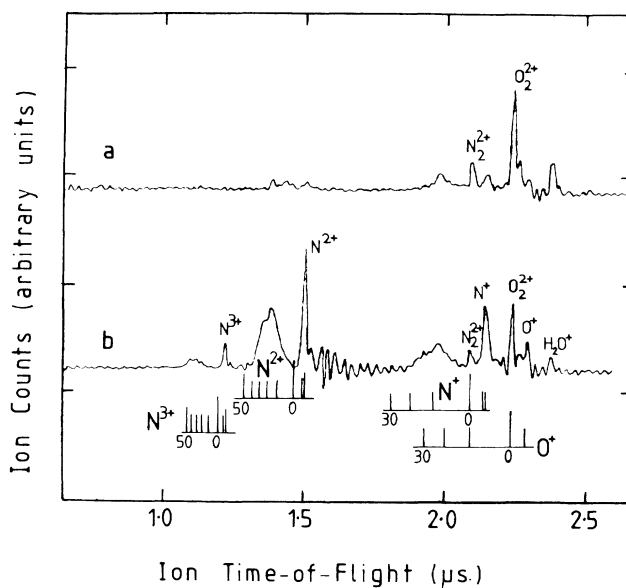


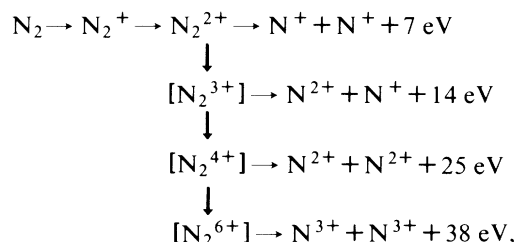
FIG. 2. The time-of-flight spectrum of air with 200 V across the 12-mm interaction region. (a) Electric field \mathbf{E} of the linearly polarized laser perpendicular to the axis of the drift tube; (b) \mathbf{E} along the drift-tube axis. The small periodic fluctuations in signal reflect the digital sampling technique.

Before discussing the dynamics of N_2 multiple ionization, it is worth noting the structure below 1 μ s in Fig. 1(a), associated with energetic protons from unidentified hydrocarbon impurities from the gas-handling system. The scale below the trace shows the kinetic-energy release in electronvolts for H^+ produced from a C—H bond. It is not yet clear what process is responsible for producing protons with such high kinetic energies.

Let us turn now to the main structures observed in Figs. 1(a), 1(b), and 2(b). Voltages of 50, 100, and 200 V, respectively, were applied across the 12-mm interaction region in order to differentiate the ions of different ionization stages and determine their energies uniquely. The measured kinetic-energy releases of the N^+ , N^{2+} , and N^{3+} ions allow us to reject two extreme hypotheses. If we assumed that all six electrons were ejected in a direct mechanism (a collective emission occurring on a time scale of ≤ 1 fs), the N^{3+} ions created at an equilibrium internuclear separation of 1.1 \AA would share an energy of about 118 eV, far in excess of the measured values. If the electrons were ejected in a "slow" sequential process, the first unstable molecular ion would completely dissociate before further ionization occurred. In this case atomic ions of all subsequent ionization stages would have the *same* kinetic energy.

In Figs. 1(a) and 1(b) there are peaks at 14 eV in *both* the N^+ and N^{2+} energy spectra and so their behavior is assumed to be correlated. There is no convincing evidence, however, for correlated N^{2+} and N^{3+} ions. This may be because N_2^{5+} dissociates completely to

N_2^{6+} . There is a peak in the N^{3+} energy spectrum at 38 eV but no such peak is evident in the N^+ or N^{2+} kinetic-energy spectra. This suggests that these energetic N^{3+} ions are the result of a Coulomb repulsion process with N_2^{6+} as parent. The above analysis leads us to suggest the following sequence of events:



where the bracket indicates a transient ion.

Although N_2^{2+} ions are known to be metastable,³ those N_2 ions involving higher stages of ionization are presumably unstable. Certainly we see no evidence of such ions with thermal energies in Figs. 1 and 2. It is therefore possible to make an estimate of the time scale of the process $N_2^{2+} \rightarrow N_2^{6+}$ denoted by the vertical arrows. We take a simple model where the two positively charged ions repel each other with a pure Coulomb force and where the electron removal is instantaneous. With the use of the experimentally observed dissociation energies given above, the transitions $[N_2^{2+}] \rightarrow [N_2^{3+}] \rightarrow [N_2^{4+}] \rightarrow [N_2^{6+}]$ are found to occur at interion separations (r) of 2.0, 2.5, and 5.5 Å, respectively. The N_2^{2+} molecular ion starts to dissociate at 2.0 Å and the times taken to increase r from 2.0 to 2.5 Å and from 2.5 to 5.5 Å are about 10 and 20 fs, respectively, giving a total time for the $N_2^{2+} \rightarrow N_2^{6+}$ sequence of about 30 fs. This is about 5 times *faster* than the equivalent process observed in Xe with use of a 0.5-ps, 192-nm laser^{4,5} (the $Xe^{2+} \rightarrow Xe^{6+}$ part of the multiple ionization process is the fastest part of the entire $Xe \rightarrow Xe^{9+}$ process). This increase in ionization rate is to be associated with the rapid increase in potential different along the molecular axis (caused by dissociation) rather than any time development of the envelope of the laser field.

A strong dependence of the amplitude of the N^{3+} peak on laser power leads us to believe that the entire sequence $N_2^{2+} \rightarrow N_2^{6+}$ occurs only at the peak of the laser pulse and in the center of the focal spot. We cannot, therefore, hope to determine the branching ratios for the horizontal-to-vertical arrow processes because some of the N^+ and N^{2+} ions may well be created outside the main focal spot and at different times within the 0.6-ps laser pulse. Under ideal circumstances this branching ratio would be a measure of the probability that a further electron be ejected from a particular transient molecular ion. Nor can we obtain unique information from the widths of the kinetic-energy distributions of the various N^{n+} ions. These widths, which increase with ionization stage, may reflect a complex interplay between

Franck-Condon overlaps, electron wave-function removal times, and oscillations of the laser field.

While the behavior of the heavy nuclei is quite well described by this simple model, that of the electrons is more problematical. The electron wave-function removal time may be comparable with the time scale of the whole process and therefore the molecular-ion stages are bracketed above. The picture of sequential multiple ionization should perhaps be replaced by a complex MEDI process. The electron configuration of N_2 is $KK2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$. The N_2^{2+} ion results from the removal of the two outer electrons. The stage $N_2^{2+} \rightarrow N_2^{6+}$ corresponds to removal of the four $1\pi_u$ electrons. If we neglected the fine structure of the $1\pi_u^4$ subshell, then a single-electron picture would envisage the wave function of all four electrons evolving in the same way under the influence of the laser field. However, we can expect that electron correlations will modify this simple picture and the short time scale of the MEDI process will add even more complexity. The whole process becomes diabatic and the Born-Oppenheimer approximation no longer applies. Clearly, the discussion of stepwise versus direct ionization^{4,6} is not closed and a more advanced, time-dependent approach is required to clarify the situation and explain the present data in detail. Apparently, at the power levels employed here, the phenomenon is molecule specific because a similar MEDI process is not observed in oxygen (see Figs. 1 and 2). Experiments using H_2 , HD, and D_2 should throw considerable light on the situation, since the theoretical treatment will be much easier in this case.

The phenomenon depicted in Figs. 2(a) and 2(b) is perfectly consistent with a classical field ionization model. Because of the molecule's shape, the potential difference created by the laser electric field E is larger along its axis than at right angles to it and thus the potential barrier to electron extraction is not so high. That is, the molecules are ionized only when their axes are close to the direction of E . The energetic ions are ejected preferentially along E since the time scale of the process is such that the molecule has no time to rotate. Figure 2(a) shows the TOF spectrum when E is perpendicular to the axis of the drift tube. The voltage applied across the interaction region is insufficient to draw the energetic ions into the detector and only thermal ions are visible. Figure 2(b) has E along the drift tube axis, as in Fig. 1, and here all forward-going ions are detected.

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