Kinetic energy distributions of ionic fragments produced by subpicosecond multiphoton ionization of N_2

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A study of the kinetic energy distributions of ionic fragments produced by subpicosecond irradiation of N_2 with 248-nm radiation at an intensity of $\sim 10^{16}$ W/cm^2 is reported. These measurements, in comparison to other findings involving molecular excitation with charged particles and soft x rays, reveal several important features of the nonlinear coupling. Four ionic dissociative channels are identified from the data on the multiphoton process. They are $N_2^{2+} \rightarrow N^+ + N^+$, $N_2^{2+} \rightarrow N + N^{2+}$, $N_2^{3+} \rightarrow N^+ + N^{2+}$, and $N_2^{4+} \rightarrow N^+ + N^{3+}$, three of which are charge asymmetric. The data for the energy distributions are found to be in approximate conformance with a simple picture involving ionizing transitions occurring within a time of a few cycles of the ultraviolet wave at an internuclear separation close to that of the ground-state ($X\,^1\Sigma_g^+$) molecule. The implication follows that a strong nonlinear mode of coupling is present which causes a high rate of energy transfer. A simple hypothesis is presented which unites the ability for rapid energy transfer with the observed tendency to produce charge-asymmetric dissociation.

I. INTRODUCTION

Processes involving the rapid production of molecular vacancies generally result in energetic fragmentation of the molecular ion produced. In particular, studies have been made of the fragmentation of N_2, having the ground-state configuration

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2 ,$$

arising from photon-induced inner-shell excitation,[1-3] electron collisions,[4] and ion collisions.[5] Rapid molecular ionization by multiphoton processes is also expected to produce ionic fragments with a characteristic distribution of kinetic energies.[6-8] Comparison of the energy spectra of the fragments produced by these different means can give information on the corresponding mechanisms of vacancy formation and the dynamics of molecular dissociation. The present study discusses the observation of N^+, N^{2+}, and N^{3+} fragments produced by multiphoton ionization of N_2 with subpicosecond 248-nm radiation at an intensity of $\sim 10^{16}$ W/cm^2. These data reveal specific information on the dynamics of these nonlinear molecular events.

Assuming that the molecular potential is dominated by the Coulomb term, the time τ for two atoms, with a reduced mass of M initially situated at a bond distance of $\sim 2\beta a_0$ and ionized suddenly by a pulse of radiation to charge states Z_1 and Z_2, to undergo a Coulomb explosion[1,9,10] and develop a separation of x, is

$$\tau \simeq \frac{\lambda\!\!\!^{-}_c}{c\alpha^2}\left[\frac{\beta^3 M}{2m_e Z_1 Z_2}\right]^{1/2} \times \left[\frac{x(1-2\beta a_0/x)^{1/2}}{2\beta a_0} + \tfrac{1}{2}\ln\left[\frac{1+(1-2\beta a_0/x)^{1/2}}{1-(1-2\beta a_0/x)^{1/2}}\right]\right] . \quad (1)$$

In Eq. (1), α is the fine-structure constant, m_e the electron mass, $\lambda\!\!\!^{-}_c$ the electron Compton wavelength, a_0 the Bohr radius, and c the speed of light. For $x = 1.0$ nm, with $M = 7$ amu, $\beta = 1$, $Z_1 = 2$, and $Z_2 = 1$, Eq. (1) gives $\tau \simeq 14.6$ fs. For these parameters, the explosion of a homonuclear diatomic molecule would yield an ion kinetic energy of $U_0 = 13.6$ eV for each fragment, a magnitude that can be readily measured. In particular, this suggests that information on electron-ionization rates in the femtosecond range associated with the production of the multiply charged ions can be obtained from the kinetic energy distributions of the ionic spectra.[6-8]

II. EXPERIMENTAL CONSIDERATIONS

In these studies of ion spectra, a subpicosecond 248-nm source[11] was used to produce the ionization in a small focal volume under collision-free conditions and the energies of the ions were measured in a time-of-flight spectrometer.[12] In the apparatus for ion detection,[13] the particles were extracted through a 0.5-mm aperture by a static field of 100 V/cm. An additional potential of 1.3

kV was applied to the ions before entering the 1-m-long free-drift region.

Several factors can contribute to the observed energy resolution of the ion signals.[14] In order to isolate the effect arising from molecular dissociation, the experiments were performed in a regime for which (1) the density was sufficiently low so that the space-charge energy was small and (2) the ion energy was sufficiently high so that the expansion of the ion packet during its flight to the detector was negligible.[14] The proper conditions were established by a study of the resolution obtained for atomic Ar, a species for which the contribution from dissociation is absent. Although the resolution limit arising from the space-charge effect deduced from the N_2^+ data was approximately 0.13 eV for our experimental conditions, the actual value was somewhat greater, since the main source of energy spreading for the energetic ions was due to the time dispersion characteristic of this technique. For 6-eV N^+ ions in our apparatus, the time dispersion is calculated to be 9.6 ns/eV. This figure, together with the electronic width of 5 ns, gives an energy resolution of $\sim$0.5 eV. Similarly, resolutions of 1.4 and 3.0 eV are obtained for 10-eV N^{2+} and 20-eV N^{3+} ions, respectively. Furthermore, the absolute energy scale is governed by the ability to determine accurately the arrival time corresponding to zero-initial-energy ions. These considerations result in experimental ion energy resolutions of $\sim$1 eV for 6-eV N^+, $\sim$2.8 eV for 10-eV N^{2+}, and $\sim$6 eV for 20-eV N^{3+}.

III. EXPERIMENTAL FINDINGS AND DISCUSSION

The time-of-flight data for the N^+-ion signal are illustrated in Fig. 1(a). Two peaks displaced symmetrically about a central component are clearly observed. Analysis of this signal shows that the prominent central feature comes from ions with a very low kinetic energy and that the two symmetrically placed components correspond to the energetic fragments generated by the molecular dissociation. This is readily seen from comparison of the data in Fig. 1(a) with that shown in Fig. 1(b) for N_2^+, an ion which should exhibit only a central thermal energy peak, perhaps involving some additional broadening arising from the effect of space charge. The two symmetrically located components of dissociative origin exhibited in Fig. 1(a) result from two velocity groups of ions, one initially headed toward the detector and a corresponding oppositely directed component whose momentum is reversed by the action of the extracting field.[2,15] Analyses of these peaks for N^+, N^{2+}, and N^{3+} have been used to determine both (a) the relative abundances and (b) the distributions of kinetic energies arising from the molecular fragmentation.

Integrated over all energies, the relative abundances in percent are 54, 32, and 14 for N^+, N^{2+}, and N^{3+}, respectively. Interestingly, the ratio $[N^+]/[N^{2+}] \simeq 1.7$, a value not far from the minimum magnitude seen ($\sim$1.9) in the soft-x-ray studies[1] slightly above the nitrogen K edge ($\hbar\omega = 440$ eV), but rather far from that observed ($\sim$4.7) well beyond the K edge ($\hbar\omega = 930$ eV) in other work.[9] A considerably higher fraction of N^{2+} appears to be produced by the multiphoton mechanism for the conditions of these experiments.

The distributions of the kinetic energies for multiphoton-produced N^+ and N^{2+} ions can be compared to the corresponding distributions observed in the soft-x-ray studies.[1-3] Figure 2 illustrates this comparison for N^+ ions which, for the x-ray work, arise from the

$$N_2^{2+} \rightarrow N^+(^3P) + N^+(^3P) \quad (2)$$

channel. All three distributions shown in Fig. 2 have their maximum strengths in the $\sim$3.9–5.0-eV range. Essentially, the same result is found in experiments involving electron[4] and ion collisions.[5] Since the energy resolution of the multiphoton data is not sufficient to exhibit the structure seen in the data produced in the x-ray studies, no significance can be attached to absence of those structured features in the multiquantum result. Overall, therefore, the gross character of the spectrum of the N^+ ions produced does not depend strongly on the

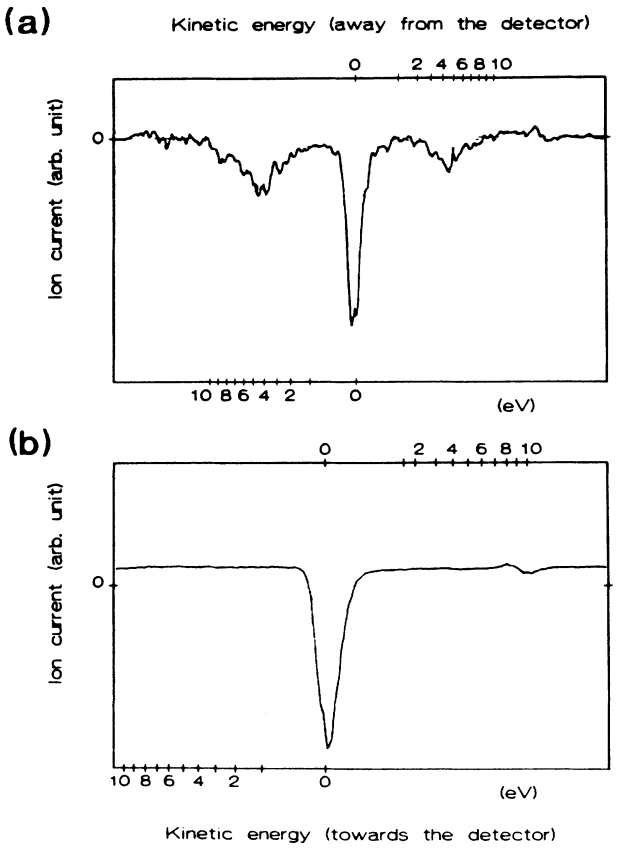

FIG. 1. (a) Time-of-flight N^+-ion signal arising from multiphoton ionization of N_2. The central feature arises from very-low-energy ions while the two symmetrically located components arise from energetic molecular dissociation from oppositely directed fragments of equal energy. See text for discussion. (b) Time-of-flight ion signal corresponding to N_2^+, a species for which the dissociative components are absent. In this case only a single peak is seen corresponding to the thermal kinetic energy of the parent N_2 molecules.

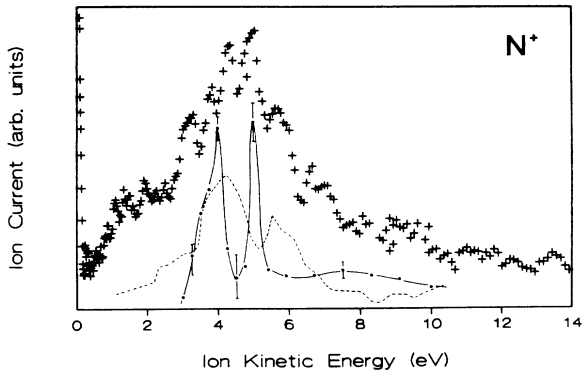

FIG. 2. Ion current (N^+) vs ion kinetic energy for N_2. The + data arise from the multiphoton ionization at 248 nm. The solid curve (ϕ) represents the results of Saito and Suzuki (Ref. 3). The dashed curve is taken from the results of Eberhardt, *et al.* (Ref. 1).

mechanism of ionization. X rays, electrons, ions, and multiphoton coupling all produce N^+ ions of approximately the same energy.

Ranked in order of ascending binding energy, the outer molecular orbitals of N_2, based on the spectroscopy[16–18] of N_2 and N_2^+, are $1\pi_u$, $3\sigma_g$, $2\sigma_u$, and $2\sigma_g$, with values of ~15.6, ~16.7, ~18.7, and ~38 eV, respectively. Consequently, these four orbitals represent two approximately separate scales of excitation with $1\pi_u$, $3\sigma_g$, and $2\sigma_u$ being the lowest, and $2\sigma_g$ the highest.

For the channel producing the N^+ ions observed, the N_2^{2+} valence holes leading to dissociation appear to be primarily of $^1\Delta_g[1\pi_u^{-2}]$ character,[19,20] the lowest-energy two-hole configuration. Since the *KVV* Auger process associated with the x-ray excitation occurs on a time short compared to molecular nuclear motions, the internuclear separation r_0 of the nascent N_2^{2+} system is expected to be very near to that given by the N_2 $X\,^1\Sigma_g^+$ ground state ($r_0 = 1.098$ Å). Therefore, the agreement of the N^+ fragment energies suggests that the multiphoton transition occurs at an internuclear separation close to the same value of r_0. Low-lying metastable states[21,22] of N_2^{2+} are presumably also formed from the decay which could account for the N^+ generation in the energy range ~2 eV.

The dominance of the $1\pi_u^{-2}$ configuration of N_2^{2+} produced by the multiquantum process is not unexpected, since it represents a rather low ionization energy and can be reached either by a direct path from N_2 $X\,^1\Sigma_g^+$ or a sequential mechanism involving the stable electronically excited N_2^+ $A\,^2\Pi_u$ state which has a $1\pi_u$ hole. A sequential mechanism proceeding through the *lowest* ion level, N_2^+ $X\,^2\Sigma_g^+$, to a $1\pi_u^{-2}$ configuration is considered unlikely, since the $X\,^2\Sigma_g^+$ state has a $3\sigma_g$ hole.[16,23] The change in the equilibrium internuclear separation of ~0.08 Å between the N_2 X and N_2^+ A states is sufficiently small to have a negligible effect on the observed kinetic energy distributions for the energy resolution used in these studies.

The production of N^{2+} ions can be considered in a similar light. In this case, the agreement represented in Fig. 2 between the x-ray-produced and multiphoton-generated N^+ distributions does *not* occur with respect to the corresponding N^{2+} kinetic energy distributions, if it is assumed that the ions arise only from the

$$N_2^{3+} \rightarrow N^{2+} + N^+ \tag{3}$$

channel. The data illustrating this comparison, which includes a fiducial signal arising form Ar^{6+}, are shown in Fig. 3. Roughly, the x-ray and multiphoton data agree for energies above ~10 eV, but deviate significantly otherwise. A substantial component of the multiphoton-generated ion signal is shifted to a considerably lower energy. Indeed, a prominent peak in the N^{2+} spectrum stemming from the nonlinear coupling is present at 6–7 eV, an energy range well below the lower limit of the soft-x-ray-produced particles.

The maximum exhibited in the 6–7-eV range in Fig. 3 for the multiquantum-produced N^{2+} ions, however, is consistent with formation by the reaction

$$N_2^{2+} \rightarrow N^{2+} + N\ , \tag{4}$$

a channel that is associated with a major feature of the Auger spectrum[2] of N_2 corresponding to a two-hole binding energy in the vicinity of ~70 eV. Indeed, in that region, the *only* decay channel observed[2] was process (3) with a characteristic N^{2+} energy of 6.7±1 eV. The N_2^{2+} states implicated,[2,20] as noted in the x-ray studies,[2] are $^1\Sigma_g[2\sigma_g^{-1},3\sigma_g^{-1}]$, $^1\Sigma_u[2\sigma_g^{-1},2\sigma_u^{-1}]$, and $^1\Pi_u[2\sigma_g^{-1}, 1\pi_u^{-1}]$. Furthermore, in those studies, spin conservation requires fragmentation from those singlet-hole configurations to excited products. The likely final states are $N^{2+}(^2P^\circ)+N(^2D^\circ)$, $N^{2+}(^2P^\circ)+N(^2P^\circ)$, and $N^{2+}(^4P)+N(^4S^\circ)$. The multiphoton data are consistent with approximately equal participation of these three channels. Interestingly, in related studies[24] of fragmentation of N_2 conducted at a wavelength of ~600 nm, process (4) was suggested in order to account for the total

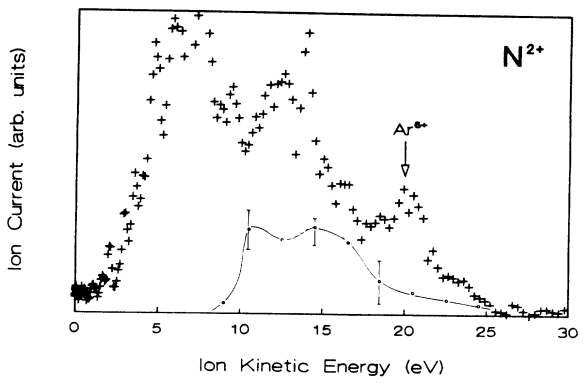

FIG. 3. Ion current (N^{2+}) vs ion kinetic energy for N_2. The + data arise from the multiphoton ionization at 248 nm which includes, as a fiducial, a component at ~20 eV produced from Ar^{6+}. The solid (ϕ) curve represents the data of Saito and Suzuki (Ref. 3) and corresponds only to the $N^{2+}+N^+$ channel. General agreement is seen except for the clear peak in the 6–7-eV region for the multiphoton data.

observed abundance of N^{2+}.

In parallel with the discussion of process (2) above, the N_2^{2+} system could be produced either by a direct mechanism from N_2 $X\,^1\Sigma_g^+$ or by a sequential mechanism involving states of N_2^+. Since N_2^+ (X) and N_2^+ (A) have $3\sigma_g$ and $1\pi_u$ holes, respectively, the production of the N_2^{2+} $^1\Sigma_g^+$ and the N_2^{2+} $^1\Pi_u$ levels given above could involve a sequential mechanism with X and A first-ion states serving as intermediate species. However, on the basis of the molecular configurations, the participation of the $^1\Sigma_u[2\sigma_g^{-1},2\sigma_u^{-1}]$ state by a sequential process would *not* be expected to occur through the X and A states. Presumably, this would require the generation of significantly more highly excited N_2^+ levels, such as the N_2^+ $B\,^2\Sigma_u^+$ which involves a $2\sigma_u$ hole.

The neutral nitrogen atoms produced by process (4) would escape detection, but a fraction of them would be expected to be converted to N^+ after dissociation by subsequent multiphoton ionization in the focal zone. The presence of such a group of 6–7-eV N^+ ions would, therefore, contribute to the signal in that range shown in Fig. 2. Since the overall $[N^+]/[N^{2+}]$ ratio is significantly greater than unity, this component of the N^+ signal is expected to be relatively small in comparison to those produced by process (2).

Alternatively, since the high-energy region of the N^+ kinetic energy distribution overlaps the low-energy region of the N^{2+} distribution, the N^{2+} seen in the 6–7-eV range could, in principle, be produced entirely by a velocity-selective conversion by multiquantum ionization of N^+ to N^{2+}. Although the multiphoton data cannot rule out this possibility, the general agreement of the N^+ and N^{2+} distributions with the corresponding ones observed in the synchrotron studies diminishes the likelihood that such a selective conversion is playing a dominant role.

A distinct group of N^{2+} ions is apparent in Fig. 3 in the 11–14-eV region for both the multiquantum and synchrotron[2,3] studies. The observation of N^{2+} with kinetic energies in the 11–14-eV range cannot plausibly be associated with channels in either N_2^+ or N_2^{2+}, even with allowance for a second step of ionization (e.g., $N^+ \rightarrow N^{2+}$) occurring after the act of molecular dissociation. The curves for these two species are simply not steep enough to give a sufficient impulse.[16,19,20] A more highly charged system, presumably N_2^{3+}, which can undergo the reaction

$$N_2^{3+} \rightarrow N^{2+} + N^+ , \tag{5}$$

is indicated. This, of course, is in agreement with the findings of the x-ray studies.[3]

For N_2^{3+}, the Coulomb term is expected to dominate the molecular curve, with the exception of relatively minor molecular contributions for internuclear separations in the ~1-Å range. The Coulombic N_2^{3+} curve indicated in Fig. 4 shows that its position is consistent with the magnitude of the observed N^{2+} kinetic energies for an approximately *vertical* excitation of the system in the potential-energy region ~84 eV. Furthermore, within the experimental resolution (~3 eV), the 11–14-eV range agrees well with the observed N^{2+} energy (~13 eV) in the soft-x-ray studies[2] stemming, in that case, from N_2^{3+}

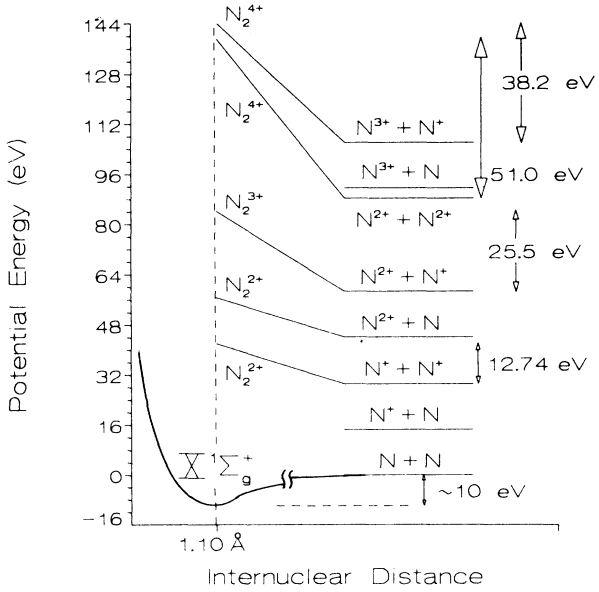

FIG. 4. A partial potential-energy diagram of N_2 indicating the ground N_2 $X\,^1\Sigma_g^+$ and the Coulombic contributions to several ionized species. Assuming vertical excitation, the ion energies observed will be one-half the amount indicated for the channels ($N^+ + N^+ \rightarrow 12.74$ eV; $N^{2+} + N^+ \rightarrow 25.5$ eV; $N^{3+} + N^+ \rightarrow 38.2$ eV). The $N^{2+} + N^{2+}$ (51.0 eV) was not observed. See text for discussion.

formation arising from a $2\sigma_g^{-2}$ level with the assumption of an additional shake-off from the first Auger event.

Overall, the observed N^+ and N^{2+} distributions, assuming that the ions arise from the decay channels $N^+ + N^+$, $N^{2+} + N$, and $N^{2+} + N^+$, all appear consistent with nearly vertical excitation of the N_2 system to corresponding N_2^{2+} and N_2^{3+} configurations. It is also known[17] that the ionic ground and low-lying N_2^+ levels ($X\,^2\Sigma_g^+$, $A\,^2\Pi_u$, and $B\,^2\Sigma_u^+$) all have equilibrium internuclear separations very close to the neutral N_2 ground state $X\,^1\Sigma_g^+$. Therefore, the removal of one electron from the neutral molecule does not cause appreciable nuclear motion or displacement. Excitation to higher-charge states, however, such as N_2^{2+} and N_2^{3+}, generally leads to unstable levels which will cause rapid motion of the nuclei. Since N_2 and N_2^+ are stable with $r_{N_2} \simeq r_{N_2^+}$ the present multiphoton data do not give information on the removal of the first electron. However, the observation of dissociative channels from N_2^{2+} and N_2^{3+} enables an estimate to be made concerning the dynamics of electron removal involving those systems.

Consider the production of N_2^{3+} from N_2^+ by the sequential mechanism

$$m_1\gamma + N_2^+ \rightarrow N_2^{2+} + e^- , \tag{6}$$

$$m_2\gamma + N_2^{2+} \rightarrow N_2^{3+} + e^- , \tag{7}$$

in which m_1 and m_2 denote the number of ultraviolet quanta involved. The observed absence of appreciable nuclear motion in the formation of N_2^{3+} can be used to estimate a residence time τ for the unstable N_2^{2+} system.

This gives an approximate figure for the electron emission rate for the physical regime being studied. For this estimate we will assume that the N_2^{2+} and N_2^{3+} molecular curves are dominated by the Coulombic interactions corresponding to $N^+ + N^+$ and $N^{2+} + N^+$, respectively. In this picture, the net change in the kinetic energy $\Delta\phi$ of the N^{2+} fragment produced by process (5) arising from a small displacement Δr in the N_2^{2+} ($N^+ + N^+$) system can be simply represented by

$$\Delta\phi = \frac{e^2}{r_0} - \frac{e^2}{r_0 + \Delta r} , \tag{8}$$

in which r_0 is the initial internuclear distance. The data indicate that

$$r_0 \simeq r_{N_2} \simeq r_{N_2^+} \simeq 1.1 \text{ Å} . \tag{9}$$

The magnitude of Δr can be derived from Eq. (8) by equating $\Delta\phi$ with the shift observed in the N^{2+} energies between the synchrotron data[2] and the multiphoton results arising from the $N^{2+} + N^+$ decay. Since no shift was observed, we use the experimental energy resolution $\Delta\varepsilon$ of N^{2+} to establish an upper bound Δr_m on this displacement. The result is

$$\Delta r_m \leq r_0 \left[\frac{1}{(e^2/r_0 \Delta\varepsilon) - 1} \right] \tag{10}$$

which, with $\Delta\varepsilon \simeq 3$ eV, gives $\Delta r_m \leq 0.33$ Å. The corresponding upper bound on the residence time τ_m of the N_2^{2+} system can be evaluated from Eq. (1) with $Z_1 = Z_2 = 1$, the parameter β selected so that

$$2\beta a_0 = r_0 , \tag{11}$$

and

$$x = r_0 + \Delta r_m . \tag{12}$$

This gives $\beta \simeq 1.04$, $x \simeq 1.43$ Å, and yields

$$\tau_m \simeq 2.35 \text{ fs} , \tag{13}$$

an interval that is only three periods of the 248-nm wave. Therefore, the ion energy distributions indicate that the lifetime of the N_2^{2+} species, as an intermediary in the production of N_2^{3+} from lower charge states (N_2 or N_2^+), is on the order of or less than approximately three cycles of the wave.

A substantial signal of N^{3+} ions was detected with the peak in the distribution occurring at ~ 20 eV as shown in Fig. 5. If we assume that the channel producing these ions is

$$N_2^{4+} \rightarrow N^{3+} + N^+ , \tag{14}$$

and further assume that the ionization occurs at the internuclear separation implied by the production of the N^+ and N^{2+} species, the energy of the N^{3+} fragment would be exactly $\frac{3}{2}$-fold the energy of the N^{2+} ion produced in the $N^{2+} + N^+$ reaction. Given the peak at ~ 12.8 eV for N^{2+} shown in Fig. 3, the expected N^{3+} kinetic energy is ~ 19.1 eV, a value very close to the measured maximum of the distribution at ~ 20 eV and indistinguishable from it with the experimental resolution pertaining to this measurement.

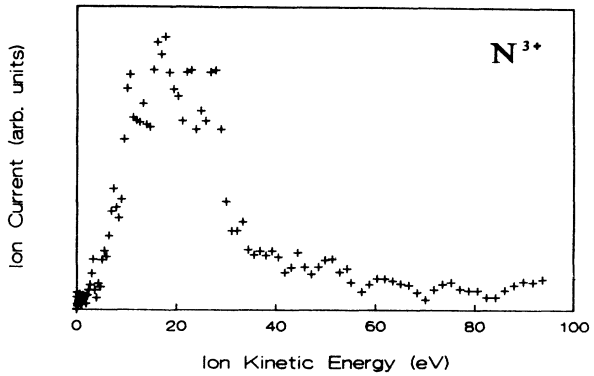

FIG. 5. Ion current (N^{3+}) vs ion kinetic energy for multiphoton ionization of N_2 at 248 nm. A prominent component exists in the 19–20-eV region.

We note that the N^+ component arising from reaction (14) is expected to be difficult to observe. The fraction of N^+ ions produced in that way is relatively small and any conversion of N^+ to N^{2+} by subsequent ionization would be effectively masked by the Ar^{6+} fiducial signal at ~ 20 eV.

Finally, if N_2^{3+} is regarded as an intermediate in the formation of N_2^{4+}, in parallel with the discussion above concerning N^{2+}-ion production following the formation of N_2^{3+}, a maximum residence time roughly comparable to that found for N_2^{2+} in Eq. (13) is found to apply.

Similar reasoning concerning the generation of N^{2+} ions from the N_2^{4+} system would place the corresponding N^{2+} energy at ~ 25 eV, a point for which no signal is evident in the distribution illustrated in Fig. 3. Apparently, the

$$N_2^{4+} \rightarrow N^{2+} + N^{2+} \tag{15}$$

channel is not dynamically favored under the conditions studied in this work, although clearly energetically accessible, since the $N^{2+} + N^{2+}$ potential lies in Fig. 4 *below* the corresponding $N^{3+} + N^+$ curve for *all* values of internuclear separation $r \geq r_0$. Interestingly, reaction (15) has been detected in other studies using covariance mapping[24] conducted under different conditions of frequency, maximum intensity, and pulsewidth. One was performed at $\sim 3 \times 10^{15}$ W/cm^2 at ~ 600 nm with 0.6-ps pulses[24] while another was conducted at $\sim 2 \times 10^{15}$ W/cm^2 at 248 nm with ~ 5-ps pulses.[25] The values of these intensities represent peak magnitudes achieved in the focus, whereas the intensity of $\sim 10^{16}$ W/cm^2 pertaining to our experiments was determined by averaging over the central Airey disk. In addition, their findings[24] indicate that the molecular transitions tend to progress in a rather less vertical fashion. Although not strictly applying to the regime studied, the Keldysh formulation indicates that either lower frequency or lower intensity would reduce the transition rate. Given this tendency, and because the cited experiments[24,25] have either one or both, it is not surprising that the ionization occurs at a somewhat

greater internuclear separation. These results point to sensitivities of the multiphoton amplitudes with respect to frequency, intensity, and pulse width which require further examination in future work.

IV. CONCLUSIONS

The kinetic energy distributions of atomic nitrogen ions produced from N_2 by multiphoton ionization reveal several characteristics of the nonlinear molecular interaction. In comparison to soft-x-ray excitation, which produces the molecular vacancies by Auger cascade and shake-off, the final configurations of the valence-shell holes produced by the multiphoton and soft-x-ray excitation appear to have many similarities.

The observed kinetic-energy distributions of the N^+, N^{2+}, and N^{3+} ions produced by the multiphoton mechanism all find consistent explanation if it is assumed that the molecular ionization for all species occurs at an internuclear separation close to the equilibrium value for neutral N_2. Namely, the transitions appear to occur nearly vertically. This finding enables an estimate of the effective residence time of intermediate molecular ionic states to be made with the outcome that this interval has an upper bound on the order of a few optical cycles for N_2^{2+} and N_2^{3+}. Since most of the deposited energy is associated with the formation of the higher-charge states, the implication is that the main energy-transfer process, when it occurs in the course of the interaction, proceeds quite rapidly. A peak energy-transfer rate on the order of a few milliwatts per molecule is inferred from these results. Therefore, a mechanism for strong coupling is presumably present.

Four molecular decay modes are identified involving molecular-ion states with a charge as high as N_2^{4+}. They are, specifically, $N^+ + N^+$, $N + N^{2+}$, $N^+ + N^{2+}$, and $N^+ + N^{3+}$. It is notable that three of these represent charge asymmetric modes and that an energetically available symmetric decay channel ($N^{2+} + N^{2+}$) was apparently not present at a detectable level. The dynamics appear to favor asymmetric channels. We observe that the enhancement of an asymmetric mode, such as $N + N^{2+}$, is a mechanism tending to cause an increase in the $[N^{2+}]/[N^+]$ fraction, a noted feature of the multiphoton data with respect to comparison with the yields observed in the synchrotron studies.

A simple hypothesis unites the rapid energy transfer, leading to vertical molecular transitions with the observed tendency to produce charge asymmetric dissociation. The presence of a large induced dipole arising from a multielectron motion will enhance the ability of the N_2 system to couple to the field. Such a dipole, however, represents a large asymmetric displacement of charge, a situation that would naturally lead to a corresponding asymmetry in the charge states of the dissociation products. This effect would be expected to be most significant for a situation involving a parallel orientation of the molecular axis along the electric vector of the ultraviolet wave.[7] In this sense, the observed charge asymmetry of the ionic products is merely a remnant of the induced electronic motions. Interestingly, the driven excursion of a free electron at $\sim 10^{16}$ W/cm^2 in a 248-nm field is ~ 8.4 Å, a value more than 7 times larger than the equilibrium internuclear separation of N_2. Even with a considerable reduction of the scale of this motion arising from the restoring binding forces in the molecule, a substantial charge displacement of the outer molecular electrons is expected under these conditions. A system behaving in this way does not decide its fate on the basis of the energy scale associated with potential final states, but rather selects the dynamical mode of interaction which favors the strongest coupling. Hints of similar behavior were seen in earlier studies of the atomic number dependence of multiphoton ionization of atoms.[26] Consequently, the final states to which such electronic motions are related become prominent in the observed distributions of the ionic products.

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