Multielectron effects in strong-field dissociative ionization of molecules

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(Received 13 March 2014; published 29 April 2014)

We study triple-ionization-induced, spatially asymmetric dissociation of N2 using angular streaking in an elliptically polarized laser pulse in conjunction with few-cycle pump-probe experiments. The kinetic-energy-release dependent directional asymmetry in the ion sum-momentum distribution reflects the internuclear distance dependence of the fragmentation mechanism. Our results show that for 5–35-fs near-infrared laser pulses with intensities reaching 1015 W/cm2, charge exchange between nuclei plays a minor role in the triple ionization of N2.

We demonstrate that angular streaking provides a powerful tool for probing multielectron effects in strong-field dissociative ionization of small molecules.

DOI: 10.1103/PhysRevA.89.043429 PACS number(s): 33.80.Rv, 34.80.Ht, 42.50.Hz, 42.65.Re

1. INTRODUCTION

Studies of intramolecular electron redistribution can provide significant insights into the understanding and control of molecule formation, chemical reactivity, and ultrafast biological signal transfer. The relevant dynamics can take place on extremely fast time scales requiring cutting-edge probe techniques. For example, attosecond intramolecular rearrangement of electrons due to the sudden removal of an electron by one high-energy photon was predicted [1] and observed using high-harmonic interferometry [2,3]. Alternatively, intramolecular electron dynamics can be probed by strong-field ionization (SFI) [4]. The SFI rate reflects strong electron-electron correlation [5] and electron localization [6–11], as well as the subsequent dynamics which are responsible for charge symmetric and asymmetric dissociation of multiply ionized molecules [12–14].

In recent pump-probe experiments, Tagliamonti et al. [15] showed that, depending on the internuclear distance, intramolecular electron redistribution can play an important role in multielectron dissociative ionization. Specifically, they considered the creation of the triply ionized dissociation channel, I2+ + I+ [denoted I2(2,1)], produced from I22+ during its expansion along a potential energy curve that asymptotically evolves into the I2+ + I channel [denoted I2(2,0)]. Surprisingly, it was determined that near the critical internuclear distance, Rc, for enhanced ionization of I22+, a field-assisted charge-transfer process plus subsequent ionization, I2(2,0) → I2(1,1) → I2(1,2) dominates over the direct ionization path, I2(2,0) → I2(2,1). At larger separations, the increased internuclear potential barrier suppresses this charge-exchange mechanism and the direct ionization I2(2,0) → I2(2,1) is favored.

In a different experiment [10], where N2 molecules were exposed to a single, spatially asymmetric two-color laser pulse, the N22+ ionic fragments from the N23+ → N22+ + N+ [denoted N2(2,1)] and N22+ → N2+ + N [denoted N2(2,0)] dissociation channels were predominantly emitted in the same direction. Those measurements are consistent with the notion that the charge-transfer depletion mechanism observed in the enhanced ionization of I22+ [15] also dominates the production of N2(2,1). Interestingly, a different phase dependence for the directional emission of N2+ from the N2(2,1) and N2(2,0) channels, not explained by the charge-exchange mechanism, was observed in another two-color experiment [16]. The discrepancy between the two-color measurements and their interpretation [10,16] might be attributed to a sensitivity of the dynamics to the frequency offset of the second-harmonic wave with respect to the fundamental [17], or to differences in the pulse duration and intensity in the two experiments. Regardless of the source, it is clear that the strong-field ionization dynamics of N2 is complex and cannot be fully characterized using two-color pulses alone.

Two-color pump-probe measurements in N2, analogous to those used to study strong-field dissociative ionization of I2 [15], might provide additional information on which ionization mechanisms dominate under different experimental conditions. However, such experiments would be extremely difficult for light molecules such as N2, due to the short time (∼25 fs) required for the dissociating molecular ion to expand to Rc [17]. Instead, we have performed two different experiments that provide sufficient temporal resolution to...
follow the dynamics leading to strong-field triple ionization of N₂. First, we have completed pump-probe measurements using 5-fs laser pulses. These pulses have an inherent spatial field asymmetry whose magnitude and direction depends on the carrier-envelope phase. In addition they can provide sufficient temporal resolution to identify when, during a dissociation event, spatial asymmetries in fragment yields arise. Second, we have employed angular streaking using elliptically polarized 35-fs pulses. Using this method, the direction of the laser field at the instant of each triple-ionization event is mapped onto the total ion momentum, while the relative momentum of the dissociating fragments reflects the molecular orientation. The variation in the fragment asymmetry as a function of kinetic-energy release (KER) reflects the ionization mechanism as a function of internuclear separation. The experiments provide no evidence for field-assisted charge-exchange processes at internuclear separations, R < R_c.

II. FEW-CYCLE PUMP-PROBE MEASUREMENT

The experimental setup for our few-cycle pump-probe measurements is schematically illustrated in Fig. 1(a) and more details can be found in Refs. [17,18]. Briefly, 5-fs, 750-nm linearly polarized pulses with energies of ~400 μJ are produced at a 3-kHz repetition rate. A portion of the beam is directed into a single-shot stereo-above threshold ionization (ATI) carrier-envelope phase (CEP) meter [19], while the rest enters a cold-target recoil-ion momentum spectrometer (COLTRIMS) [20]. A split mirror within the COLTRIMS chamber separates that beam into pump-probe pairs and focuses them with intensities of ~(0.5–1) × 10^15 W/cm² into a N₂ gas jet. The momenta of the fragment ions and the laser CEP are determined for each laser shot as the pump-probe delay is scanned.

Interestingly, the few-cycle pump-probe experiments show that ionization from N₂(2,0) channels is an important pathway in producing N₂(2,1). Figure 2 shows the KER associated with the production of N₂⁺ ions as a function of the pump-probe delay. At long delays the yields are delay independent and distinct KER bands, corresponding to ejection into the N₂(2,0) channel at 4–6 eV and the N₂(2,1) channel at 13–21 eV, are clearly visible. Near 25 fs, the N₂(2,0) channel is strongly depleted by the probe and a delay-dependent feature appears. The delay dependence reflects the additional KER obtained when fragments dissociating on the N₂(2,0) curve are further ionized at ever-increasing internuclear separations, and is
similar to that attributed to enhanced ionization as probed with longer pulses in I$_2$ [9]. As shown in Fig. 3, using ion-ion coincidence we can confirm that the delay-dependent feature extends from ~10 to 45 fs and is associated with N$_2$(2,1) dissociation. Moreover, by computing the expected delay-dependent KER from model N$_2$(2,0) and N$_2$(1,1) potential curves [17], we conclude that this N$_2$(2,1) channel is produced directly via probe ionization of molecular ions dissociating along a N$_2$(2,0) curve (Fig. 3). No evidence for the production of N$_2$(2,1) during the dissociation of N$_2$(1,1) is seen. To reproduce the observed KER in the N$_2$(1,1), N$_2$(2,1), and N$_2$(2,2) channels, the model assumes that double ionization occurs at R = 3 a.u. and that dissociation proceeds along Coulombic N$_2$(1,1) and flat N$_2$(2,0) potential curves. It is worth noting that while precise predictions for the N$_2$(2,0) curve are not available, our approximation of a flat potential is in qualitative agreement with recent estimates [21]. Also, the use of a Coulombic form for the N$_2$(1,1) curve neglects attractive well features at small R [21] and, therefore, likely overestimates the KER that would result from ionization out of this channel at small R, i.e., for delays <15 fs. However, it will have little influence on the prediction for large delays where the differences between the measured KER release and the dashed line prediction are significant.

Notably, the few-cycle pump-probe experiments did not detect any directional emission of N$_2^{2+}$ fragments from N$_2$(2,0) or N$_2$(2,1) as a function of the laser CEP [17]. This suggests that a field asymmetry must be present for an extended period during the dissociation to induce directional emission of N$_2^{2+}$ fragments and, accordingly, that few-cycle pulses induce ionization dynamics following a different pathway.

### III. Angular Streaking Measurement

To further elucidate the mechanism that is responsible for triple-ionization-induced dissociation of N$_2$ into the N$_2$(2,1) channel, as shown in Fig. 1(b), we applied the angular streaking technique [11,22–27] and COLTRIMS [20] using single-color, elliptically polarized pulses. Laser pulses (35 fs, 790 nm, polarization ellipticity $\epsilon \approx 0.68$) from an 8-kHz Ti:sapphire multipass amplifier were focused by a concave mirror ($f = 7.5$ cm) into a supersonic N$_2$ gas jet in the vacuum chamber. Ion fragments produced via SFI were detected by a time- and position-sensitive microchannel plate detector [28] located at the end of the spectrometer, allowing us to reconstruct the three-dimensional momenta of the fragments.

As we will show in the following, by selecting the departing direction of N$_2^{2+}$ along the major polarization axis, an asymmetry of the sum-momentum distribution of the ion fragments of N$_2$(2,1) along the minor polarization axis is observed. The KER dependence of this asymmetry allows us to probe the production of N$_2$(2,1) from N$_2$(2,0) as a function of internuclear distance during the molecular expansion in a multicycle laser pulse. We find that under our experimental conditions, N$_2$(2,1) is primarily produced from N$_2$(2,0) in a one-electron process. The third electron is ejected directly into the continuum during the expansion of the N$_2^{2+}$ along an asymptotic N$_2$(2,0) potential energy curve. Most of the N$_2$(2,1) fragments are produced at $R < R_c$ and, apparently, the charge-transfer mechanism plays little if any role.

To probe the ionization dynamics using angular streaking, both the relative and sum momenta of the ion fragments from the N$_2$(2,1) channel are measured. These reveal the orientation of the molecule and the instantaneous laser field at the ionization, respectively. As illustrated in Fig. 1(b), the major and minor field axes of the elliptically polarized pulse lie along the $y$ and $z$ axis, respectively. Since the tunneling rate depends exponentially on the field strength, ionization occurs predominantly at the field maxima, i.e., when the field points toward $+y$ or $-y$, leading to a final momentum of the released electron along $+z$ or $-z$ due to angular streaking in the counterclockwise rotating laser field. Due to momentum conservation, the total momentum of the fragment ions receives a boost along $-z$ or $+z$ as they recoil from each freed electron.

In addition to the center-of-mass motion of the molecular ion due to the net recoil from the ejected electrons, the ionic cores repel each other along the internuclear axis, yielding a much larger relative momentum $(p_{rel})$ along that axis. Due to this large momentum, the axial recoil approximation holds, and the spatial orientation of the molecular ion during the laser pulse is mapped onto the relative momentum of the fragments. To achieve the best momentum resolution, the $z$ axis is oriented along the time-of-flight direction of the spectrometer, while the supersonic molecular jet propagates along the $y$ axis. Since the charge-transfer effect [15] and electron-localization-assisted enhanced ionization are only active for molecules aligned along the ionizing field [6,7,9,10], we restrict our data analysis and discussion to ions ejected within a 45° cone centered on the major polarization (i.e., $y$) axis.

The ion sum-momentum distribution $p_z$ of the N$_2$(2,1) ion fragments created by counterclockwise and clockwise rotating elliptically polarized fields is plotted in Figs. 4(a) and 4(b), respectively. The elliptically polarized laser pulse sequentially removes three electrons by suppressing the recoil process [22]. In this experiment, two electrons
are initially liberated at or near the equilibrium internuclear separation, $R_c$. The N$_2^{3+}$ ions then dissociate along the potential energy curve asymptotically associated with N$_2$(2,0). At some time during the dissociation, a third electron can be released, resulting in subsequent motion in a N$_2$(2,1) channel. Due to the angular streaking of the rotating laser field, the N$_2^{3+}$ is emitted toward $-y$ or $+y$, respectively; i.e., when the third electron is preferentially ionized by a laser field pointing toward $+y$ or $-y$, respectively. This indicates that N$_2$(2,1) is predominantly produced from N$_2$(2,0) by directly releasing the third electron into the continuum without intramolecular charge redistribution. Figure 4(b) shows the same curves recorded with the opposite helicity, i.e., with a clockwise rotating laser field. Inversion of the helicity should reverse the angular streaking result. Indeed, the spectra plotted in Figs. 4(a) and 4(b) are near-mirror images of each other, supporting the validity of this interpretation.

To obtain a more quantitative understanding of the data, we fit the ion sum-momentum distribution $p_{z_{\text{sum}}}$ as a convolution of the momenta of the released three electrons [23],

$$p_{z_{\text{sum}}}(p_z) = \frac{1}{\sqrt{2\pi} \sigma_{123}} \sum_{i,j,k} A_{123ijk} \exp\left[-0.5(p_z - p_{z_{123ijk}})^2/\sigma_{123}^2\right],$$

where $A_{123ijk} = A_i A_j A_k$, $\sigma_{123}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2$, and each freed electron is assumed to have an independent Gaussian momentum distribution, $n_i/\sigma_n \sqrt{2\pi} \exp[-0.5(p_z - p_{z_{\text{sum}}})^2/\sigma_n^2]$, where $n = 1, 2, 3$ denotes the first, second, and third electron, respectively. From the fit to the data plotted in Fig. 4(a) (solid blue curve), we determine the average momenta of the electrons: $p_{z_{123}} = 1.04 \pm 0.02$, $p_{z_{12}} = 1.41 \pm 0.04$, and $p_{z_{23}} = 1.26 \pm 0.05$ a.u. The three average momenta are uniquely assigned under the following assumptions. First, the asymmetry with respect to the sign of $p_{z_{\text{sum}}}$, observed in the emission of N$_2^{3+}$ fragments toward $-y$ or $+y$ (Fig. 2), is due solely to the momentum imparted to the third electron. Second, since the sequential ionization of the second electron occurs at a higher intensity than the first ionization, the average drift momentum of the second electron must be higher than the first.

As shown in Fig. 2, it takes $\sim 25$ fs for the dissociating N$_2^{3+}$ ions to reach $R_c$ where the probability for additional ionization is maximized. The KER for N$_2$(2,1) formed at $R_c$ is $\sim 12$ eV. This is close to the minimum KER that is observed with 35-fs elliptically polarized pulses. Apparently, the expanding molecular ion reaches $R_c$ during the falling edge of the 35-fs pulse, when there is insufficient intensity to induce triple ionization at $R_c$ in spite of the maximal enhancement in the ionization rate there. Thus, the third electron is most likely released at an intermediate separation, $R_0 < R < R_c$. It therefore gains a relatively small momentum from the rotating laser field as compared to the second electron, which is released nearer to the intensity peak of the laser pulse. Although the symmetry of the ionizing orbital may play a role in the predominant mechanism (direct or charge-transfer-assisted enhanced ionization) responsible for the creation of N$_2$(2,1) during dissociation in the N$_2$(2,0) channel can be determined from the emission direction of the N$_2^{3+}$ fragment from N$_2$(2,1) along the major polarization axis, and the ion sum-momentum distribution of the ionic fragments along the minor polarization axis.
initial ionization step, we observe that the triple-ionization probability is significantly enhanced when the molecule aligns along the major polarization axis for the whole KER range of the N$_2$(2,1) channel. This indicates a substantial influence by the laser field on the angular distribution when the molecular ion expands with no discernible role of the field-free symmetry of the molecular orbitals.

To better characterize the triple-ionization mechanism we define an asymmetry parameter, $\beta = (A_{+y} - A_{-y})/(A_{+y} + A_{-y})$, as the normalized difference in the probabilities that the third ionization event occurs with the laser field along $+y$ and $-y$ for a given emission direction of N$_2^+$. For a counterclockwise rotating laser field we expect $\beta < 0$ ($>0$) if the ionization occurs via a direct process for N$_2^+$ ions emitted along $+y$ ($-y$). Conversely, if the charge-transfer mechanism dominates, $\beta$ should have the opposite sign. By fixing the fitting parameters of the first two electrons, we find an asymmetry parameter, $\beta = -0.168 \pm 0.005 (0.127 \pm 0.005)$, for the N$_2^+$ ions emitted toward $+y$ ($-y$), in a counterclockwise rotating laser field. Clearly, the direct mechanism dominates the triple-ionization process under our experimental conditions.

Interestingly, as shown in Fig. 5(a), the N$_2$(2,1) channel has a broad KER distribution, extending from 12 to 24 eV in the angular streaking experiments. Since the KER depends on the internuclear separation at the instant of ionization, the KER distribution can be used to investigate the ionization mechanism as a function of $R$.

The open squares in Fig. 5(b) show the dependence of the asymmetry parameter on KER. The positive asymmetry which reflects direct single-electron ionization for N$_2^+$ emitted toward $-y$ in a counterclockwise rotating laser field, is observed for KER < 18.5 eV, i.e., for large internuclear distances. The asymmetry parameter approaches zero for larger KER, i.e., smaller internuclear distances. The ion sum-momentum distributions at small and large KER are plotted in Figs. 5(c) and 5(d), respectively. The absence of asymmetry for small internuclear distances is consistent with the lack of fragment asymmetry observed with few-cycle laser pulses. Both asymmetries require some degree of electron localization to define the orientation of a particular fragment at the instant of the ionization event of interest. This localization does not fully occur until the molecular ion has expanded to near $R_c$.

In addition to the asymmetry, we plot the fitted momentum $p_{z3}$ of the third electron as filled blue squares in Fig. 5(b). It can be seen that $p_{z3}$ increases with increasing KER. This provides further support for the notion that the molecular ion begins to expand at some time near the intensity peak of the laser pulse. If the third electron ionizes at this time, higher laser intensities are available for the ionization and the field imparts a larger average drift momentum. Moreover, at these small internuclear separations, enhanced ionization cannot efficiently occur and a higher field intensity is required to ionize the third electron. Nearer to $R_c$, the ionization rate increases considerably, so lower laser intensities can efficiently ionize the third electron. Indeed, the lower momentum transfer observed for larger internuclear separations indicates that the third electron escapes into the continuum at relatively low intensity, assisted by electron localization, as $R$ approaches $R_c$ during the falling edge of the laser pulse.

**IV. CONCLUSIONS**

In summary, we have used angular streaking and few-cycle pump-probe experiments to probe dissociation following triple ionization of N$_2$. For our experimental conditions, the N$_2$(2,1) channel is produced either by directly releasing three electrons around the equilibrium internuclear distance of N$_2$ (resulting in a large KER), or through direct ionization of the third electron as the molecular ion expands toward $R_c$. The charge-transfer mechanism described in [15] plays a minor, if any, role. This may be due to the fact that the laser has insufficient intensity to perform the final ionization step when the molecule reaches $R_c$. The angular streaking technique in conjunction with results from the time-resolved experiments utilizing few-cycle pulses provides a powerful tool to probe coupled dynamics of electrons and nuclei during strong-field ionization of small molecules. In the future, angular streaking might be directly implemented in a pump-probe configuration with ultrashort pulses to visualize intramolecular electron motion.

**ACKNOWLEDGMENTS**

This work was supported by the “Eastern Scholar” Program, the NCET in University (Grant No. NCET-12-0177), the Projects from SSTC (Grant No. 13QH1401400), the “Shu Guang” project (Grant No. 12SG25), the National Natural Science Fund (Grants No. 11374103 and No. CHE-0822646), the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science,