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Dynamics of triple-ionization-induced dissociation in diatomic molecules in strong fields

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In this paper, we report the first comparison study between N_2 and O_2 on their triple-ionization-induced dissociation channels using near-IR 800-nm ultrashort laser pulses. Our experiment shows that the $O^{2+}+O^+$ channel is predominately formed nonvertically through the intermediate O^++O^+ channel, while the $N^{2+}+N^+$ channel appears to be formed vertically at the lower intensity range but nonvertically at higher intensities. Interestingly, $N^{2+}+N^+$ appears to be in the electronically excited state when it is reached vertically in the lower intensity range. The different triple ionization and dissociation behaviors between N_2 and O_2 can be understood by considering the ionization dynamics of the two molecules in our ultrashort laser pulses.

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The study of dissociation dynamics from a multiply charged molecular ion has attracted much attention in the strong field regime when the laser field strength is strong enough to ionize many electrons during the short interaction time (femtosecond time scale) [1–13]. In the past, two mechanisms have been suggested to explain the dissociation dynamics from multiple charged molecular ions, vertical transition and nonvertical transition. Taking a triply ionized diatomic molecular ion ${X_2}^{3+}$ as an example, in the vertical transition, ${X_2}^{3+}$ is reached directly from the neutral molecule X_2 and then dissociates into atomic ions $X^{2+}+X^+$ with a high kinetic energy release due to a strong Coulomb explosion from the equilibrium internuclear separation [1,2]. In the nonvertical transition, X_2 can be first doubly ionized and starts to dissociate to two X^+ ions. As the laser intensity continues to rise, a third electron may be ionized resulting to the $X^{2+}+X^+$ channel [3–7]. This nonvertical stepwise process will lead to a smaller kinetic energy release.

Both vertical and nonvertical transitions have been observed in studying the dissociation dynamics of triply ionized N_2 molecules [3–6]. In studies using quasimonochromatic soft x ray [1] and 248-nm 0.6-ps intense laser pulses [2], the $N^{2+}+N^+$ dissociation channel is believed resulting from the vertical transition to ${N_2}^{3+}$ due to a large kinetic energy release (~26 eV). In contrast, however, a relatively small kinetic energy of 12–16 eV was found associated with the $N^{2+}+N^+$ dissociation channel in experiments using 0.6-ps pulses at a wavelength of 600 nm, 1.2-ps pulses at a wavelength of 248 nm, and 2-ps pulses at wavelengths of 305 and 610 nm [3–6]. It was suggested in the latter experiments that the smaller kinetic energy release could be explained by the nonvertical transition: once double ionization has occurred, the N^+ ions will start to move apart. As the laser intensity continues to rise, a third electron may be removed and the dissociation will move to the $N^{2+}+N^+$ repulsion curve, and this nonvertical stepwise process will lead to a smaller kinetic energy release. We can see that both vertical and nonvertical transitions have been seen under similar experimental conditions (e.g., in 248-nm radiation [2,4]) and therefore, it is unclear under what conditions one type of transition will be favored over the other one in forming $N^{2+}+N^+$.

Comparison studies of N_2 and O_2 have helped us gain much insight in phenomena involving single- and double-electron strong field ionization and dissociation [11–13]. In this paper, we extend the comparison study of N_2 and O_2 to the triple-ionization-induced dissociation channels. Using 60-fs ultrashort pulses at 800 nm, our study shows that there is a clear signature of vertical transition in the formation of the $N^{2+}+N^+$ channel, while the $O^{2+}+O^+$ channel mainly results from nonvertical transition through the O^++O^+ channel.

The laser used in the experiment is an amplified Ti:sapphire system consisting of a mode-locked oscillator and a two-stage amplifier (a regenerative amplifier and a two-pass external amplifier). After final pulse compression, the system generates 60 fs pulses of about 1.2 mJ/pulse at a 1 kHz repetition rate with the central wavelength at 800 nm. A thin lens is used to focus the beam into the target chamber. The dispersion introduced from the optics and the chamber window is precompensated by introducing an additional negative chirp at the compressor after the amplifier. The chamber base pressure is $<5.0\times10^{-10}$ Torr. Experimentally, a standard time-of-flight (TOF) mass spectrometer is used for ion collection and detection. At the end of the TOF, ions are detected with a microchannel plate as a function of flight time. This signal is further amplified, discriminated, and either integrated with a boxcar to produce ion yields or sent to a multihit time digitizer to generate TOF mass spectra. The time digitizer used (ORTEC model 9353) provides an ultrahigh resolution of 100 ps of the flight time. The laser field is linearly polarized with the polarization parallel to the TOF axis. The TOF voltage plates for extracting and accelerating ions each has only a 1 mm pinhole opening to allow ions to pass through. High-precision ionization yield measurements of different molecular species are essential in order to compare different channels. Using a technique described in Ref. [13], we are able to accurately determine the flight time and width of a certain species and isolate it from contamination from adjacent peaks.

Figure 1 shows the TOF mass spectra across the delay range corresponding to the dissociation channels of $N^{2+}+N^+$ and $O^{2+}+O^+$. All dissociation channels have a double peak structure corresponding to the ions with initial velocity towards and away from the microchannel plate detector at

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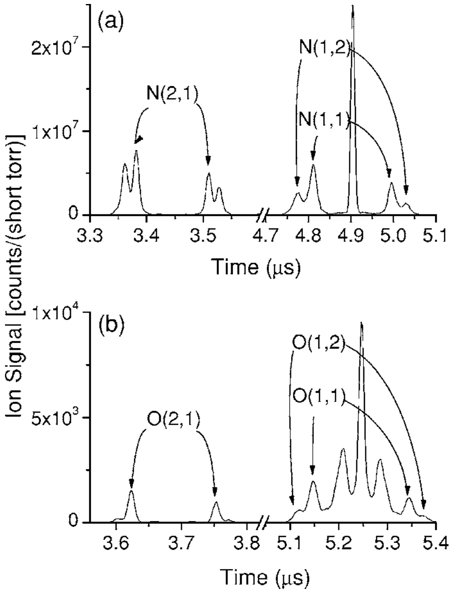

FIG. 1. Time-of-flight spectra of (a) N^+ and N^{2+} channels and (b) O^+ and O^{2+} channels with linear polarized light.

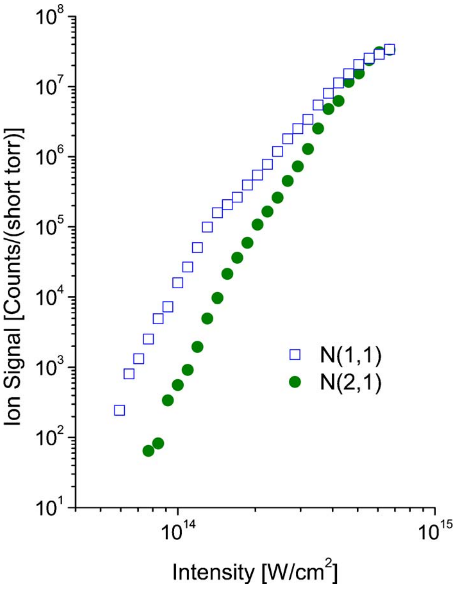

FIG. 2. (Color online) Ion yields for N^{2+} from N(2,1) and N^+ from N(1,1) with linearly polarized light.

the end of the TOF drift tube. To identify different dissociation channels, an ion-ion correlation technique is used, as described in detail in Ref. [13]. Note, throughout this paper we will label N^+ and N^{2+} from the dissociation channel $N^+ + N^{2+}$ as N(1,2) and N(2,1). Since N(1,2) and N(2,1) are from the same parent ion, we will only discuss one of these two species. We choose to study N(2,1) here because the N(2,1) peak is cleaner in its surrounding TOF spectral background. Similarly, we will use O^{2+} to represent the $O^+ + O^{2+}$ channel and O^{2+}will be labeled as O(2,1) throughout the paper. The initial kinetic energy of a dissociating ion can be determined from the flight time separation of the dissociating ion pair in a TOF spectrum. The total kinetic energy release of the N^{2+} and N^+ channel is determined to be 15.0 eV by summing the kinetic energy carried by the corresponding N^{2+} and N^+ ions. Apparently, the observed kinetic energy release in our near-IR laser fields is much lower than the high-energy photon experiments in Refs. [1,2] but is similar to the experiments considering N(2,1) being reached through the nonvertical transition [3–6].

It is natural to think that the low dissociation energy of the N(2,1) channel is also reached from a nonvertical transition. However, the pulse duration in our experiments is significantly shorter than in previous work (>500 fs). In the nonvertical transition, double ionization of N_2 needs to start on the rising edge of the pulse. As the two N^+ ions repel and separate from each other, it requires that the laser intensity continue to rise and at a certain internuclear distance, the laser field will remove the third electron and the dissociation will move to the $N^{2+}+N^+$ repulsion curve. This nonvertical transition is relatively easy to achieve using a long pulse, as in Refs. [3–6]. However, it is unclear if the continuous increase of the laser intensity required to produce the $N^{2+} + N^+$ channel nonvertically can be readily realized using our ultrashort laser pulses.

Indeed, the question of whether we produce the $N^{2+}+N^+$ channel vertically or nonvertically can be answered experimentally by utilizing a well-established technique [11–13] from the study of sequential versus nonsequential ionization by analyzing the intensity dependence of the ion yield ratio curve, where the intensity dependence can reflect if double ionization proceeds through single ionization. In our case, we will analyze the intensity dependent ratio curves of N(2,1)/N(1,1) and O(2,1)/O(1,1), where N(1,1) and O(1,1) denote the $N^+ + N^+$ channel and the $O^+ + O^+$ channel, respectively. Take N(2,1)/N(1,1) as an example: if N(2,1) is produced through the intermediate state N(1,1), the ratio N(2,1)/N(1,1) will have a strong intensity dependence. However, if this ratio depends only weakly on intensity, it shows that the precursor to N(2,1) is not N(1,1). Figure 2 shows the ion yields of N^{2+} from N(2,1) and N^+ from N(1,1), and Fig. 3 shows the ion yields of O^{2+} from O(2,1) and O^+ from O(1,1) with linear polarized light. The intensity dependent ratio curves of N(2,1)/N(1,1) and O(2,1)/O(1,1) are plotted in Fig. 4. It appears that the ratio curve of N(2,1)/N(1,1) has a weaker dependency on intensity than O(2,1)/O(1,1) below the intensity of 2.8×10^{14} W/cm^2, as shown in Fig. 4. This indicates that the vertical transition plays a significant role in forming N(2,1) in this intensity range. However, the kinetic energy release of the $N^{2+}+N^+$ channel in our experiment (15.0 eV) is significantly lower than the value expected from a vertical transition (~26 eV). Therefore, if the N(2,1) channel in our experiment results from the vertical transition, the final atomic ions must be in highly excited states [~11 eV above the ground state of N(2,1)]. Recently, there have been a number of experimental studies indicating that molecular ions often reside in their excited states following ultrashort pulse excitation [12,14,15], and this is consistent with what we see here in the $N^{2+}+N^+$ channel. The possible final excited states in our experiments are $N^{2+}(^4P)+N^+(^1S)$ and $N^{2+}(^2P^o) + N^+(^3D^o)$, whose threshold energies are about 11.14 and 11.43 eV higher than the ground state of the dissociating

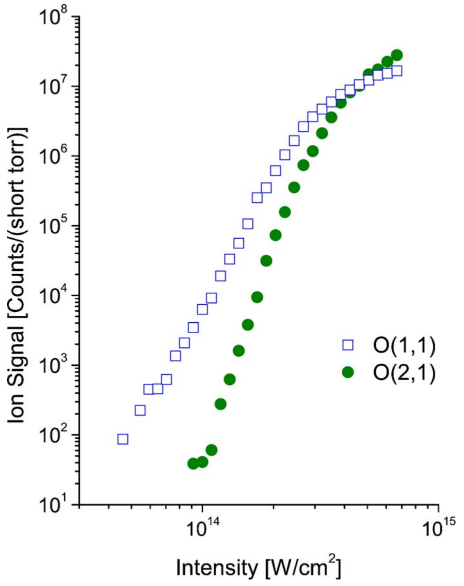

FIG. 3. (Color online) Ion yields for O^{2+} from O(2,1) and O^+ from O(1,1) with linearly polarized light.

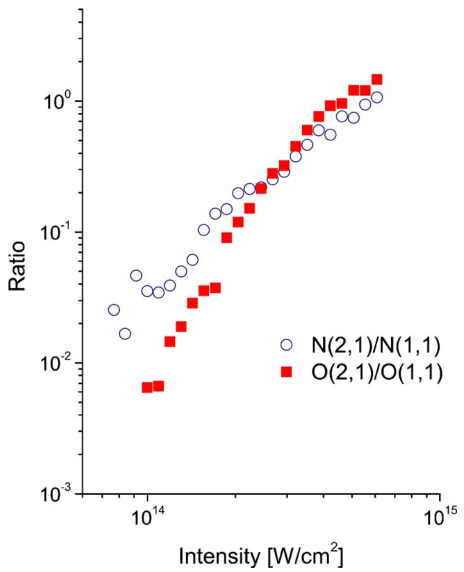

FIG. 4. (Color online) Intensity dependent ratio curves for N(2,1)/N(1,1) and O(2,1)/O(1,1).

channel $N^{2+}(^2P^o)+N^+(^3P)$, respectively. In contrast to N(2,1), the ratio curve of O(2,1)/O(1,1) drops monotonically with decreasing intensity and therefore, the formation of O(2,1) should proceed through O(1,1). The kinetic energy release of the O(2,1) channel is measured to be 13.8 eV [7], which is about 6.0 eV higher than the O(1,1) channel in our experiment. Based on this kinetic energy release, we estimate that the third electron ionization occurs at a distance of about 2.4 Å [7].

From Fig. 3, we can see that the difference between ion yields of O(2,1) and O(1,1) decreases with increasing intensity. Despite the fact that the threshold energy for O(2,1) is about 35.12 eV above the O(1,1) channel, the ion yield of O(2,1) surpasses that of O(1,1) at intensities above 4.0×10^{14} W/cm^2. It appears that O(2,1) starts to deplete O(1,1) at this high intensity range, further confirming our belief that O(1,1) is the precursor to O(2,1). Similar competing behavior is also seen between the N(1,1) and N(2,1) channels at the higher intensity range, as shown in Fig. 2, indicating that N(2,1) may also proceed through N(1,1) at the higher intensity range. This can be seen more clearly from Fig. 4 that the intensity dependence of N(2,1)/N(1,1) is stronger above 2.8×10^{14} W/cm^2 but weaker below this intensity, indicating that N(2,1) is more likely reached vertically at the lower intensity range but starts to proceed through N(1,1) as the intensity increases. This is indeed reasonable because at lower intensities, the criterion of the continuous increase of laser intensity in order to produce $N^{2+}+N^+$ nonvertically may not be realized using our ultrashort laser pulses. Therefore, the only way to create $N^{2+}+N^+$ is through the vertical transition. As intensity increases, however, double ionization of N_2 will start to occur at an earlier time during the rising edge of our pulse and nonvertical transition to access the $N^{2+}+N^+$ channel may become possible. This picture can also explain why $O^{2+}+O^+$ is always formed nonvertically. Since the dissociative double ionization potential of O^++O^+ is less than N^++N^+, double ionization of O_2 can occur earlier in the pulse rising edge, allowing the nonvertical transition to access the $O^{2+}+O^+$ channel. Note, the ionization potential from the ground state of a neutral molecule to a dissociating fragment is determined by summing the following contributions: the energy necessary to dissociate the neutral molecule, the energy needed to ionize each atom to its specific charge state, and the released kinetic energy [13]. The ionization potentials obtained by this method in our experiment for N(1,1) and O(1,1) are 46.6 and 40.1 eV, respectively, above the ground states of the neutral molecule.

In summary, we perform the first comparison study between N_2 and O_2 on their triple-ionization-induced dissociation channels using near-IR 800-nm ultrashort laser pulses. The $O^{2+}+O^+$ channel is predominately formed nonvertically through the intermediate O(1,1) channel, while the $N^{2+}+N^+$ channel appears to be formed vertically at the lower intensity range but nonvertically at higher intensities. Interestingly, $N^{2+}+N^+$ appears to be in the electronically excited state when it is reached vertically in the lower intensity range and thus giving a relatively small kinetic energy release. This is consistent with a number of previous observations that molecular ions often reside in their excited states following ultrashort pulse excitation [12,14,15] but more likely in the ground state using long pulses [3–7]. The different triple ionization and dissociation behaviors between N_2 and O_2 can be understood by considering the ionization dynamics of the two molecules in our ultrashort laser pulses.

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[1] W. Eberhardt, E. W. Plummer, I. W. Lyo, R. Carr, and W. K. Ford, Phys. Rev. Lett. **58**, 207 (1987).

[2] K. Boyer, T. S. Luk, J. C. Solem, and C. K. Rhodes, Phys. Rev. A **39**, 1186 (1989).

[3] L. J. Frasinski, K. Codling, P. Hatherly, J. Barr, I. N. Ross, and W. T. Toner, Phys. Rev. Lett. **58**, 2424 (1987).

[4] M. Stankiewicz, L. J. Frasinski, G. M. Cross, P. A. Hatherly, K. Codling, A. J. Langley, and W. Shaikh, J. Phys. B **26**, 2619 (1993).

[5] C. Cornaggia, J. Lavancier, D. Normand, J. Morellec, and H. X. Liu, Phys. Rev. A **42**, 5464 (1990).

[6] K. Codling, L. J. Frasinski, and P. A. Hatherly, J. Phys. B **22**, L321 (1989).

[7] D. Normand, C. Cornaggia, J. Lavancier, J. Morellec, and H. X. Liu, Phys. Rev. A **44**, 475 (1991).

[8] T. Seideman, M. Yu. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).

[9] G. L. Kamta and A. D. Bandrauk, Phys. Rev. Lett. **94**, 203003 (2005).

[10] A. S. Alnaser, C. M. Maharjan, X. M. Tong, B. Ulrich, P. Ranitovic, B. Shan, Z. Chang, C. D. Lin, C. L. Cocke, and I. V. Litvinyuk, Phys. Rev. A **71**, 031403(R) (2005).

[11] C. Guo, M. Li, J. P. Nibarger, and G. N. Gibson, Phys. Rev. A **58**, R4271 (1998).

[12] C. Guo, M. Li, and G. N. Gibson, Phys. Rev. Lett. **82**, 2492 (1999).

[13] C. Guo, M. Li, J. P. Nibarger, and G. N. Gibson, Phys. Rev. A **61**, 033413 (2000).

[14] J. P. Nibarger, M. Li, S. Menon, and G. N. Gibson, Phys. Rev. Lett. **83**, 4975 (1999).

[15] L. Quaglia and C. Cornaggia, Phys. Rev. Lett. **84**, 4565 (2000).