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Triple-ionization-induced dissociation of NO in strong laser fields

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In this paper, we study the dynamics of triple-ionization-induced dissociation in a heteronuclear diatomic molecule NO. Compared to homonuclear diatomic molecules, NO shows a greater complexity in its final states following triple ionization. By utilizing a well-established technique from the study of sequential versus nonsequential ionization, our study shows that both the $N^{2+}+O^{+}$ and $N^{+}+O^{2+}$ channels are predominately formed nonvertically through a relatively slowly dissociating $N^{+}+O^{+}$ state. Finally, we show that both the $N^{2+}+O^{+}$ and $N^{+}+O^{2+}$ channels are formed at nearly the same internuclear separation that is much smaller than the critical internuclear distance, indicating that dissociative ionization of high charge states in a molecule can occur as a molecule steadily expands from its equilibrium separation rather than always at the critical internuclear distance.

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The study of multielectron dissociative ionization of molecules 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) [1–8]. Multielectron dissociative ionization can be induced by two types of transitions, vertical and nonvertical. Taking a triply ionized diatomic molecular ion, XY^{3+}, as an example, in the vertical transition, XY^{3+} is reached directly from the neutral molecule XY and then dissociates into either the $X^{2+}+Y^{+}$ or $X^{+}+Y^{2+}$ state with a high kinetic energy release due to a strong Coulomb explosion from the equilibrium internuclear separation [1,2]. In the nonvertical transition, XY can be first doubly ionized and starts to dissociate to X^{+} and Y^{+} ions. As the laser intensity continues to rise, a third electron may be ionized, resulting in the $X^{2+}+Y^{+}$ or $X^{+}+Y^{2+}$ state [3–6]. This nonvertical stepwise process will lead to a smaller kinetic energy release with $X^{+}+Y^{+}$ as an intermediate state. Recently, we performed a study on triple-ionization-induced dissociation in homonuclear diatomic molecules, N_2 and O_2 [9]. Our study shows that both vertical and nonvertical transitions are commonly seen in homonuclear diatomic molecules: $O^{2+}+O^{+}$ is predominately formed nonvertically through the intermediate $O^{+}+O^{+}$ channel, while $N^{2+}+N^{+}$ is formed vertically at the lower intensity range but nonvertically at higher intensities [9].

In this paper, we extend the study on the dynamics of triple-ionization-induced dissociation to heteronuclear diatomic molecules. In contrast to homonuclear molecules, heteronuclear diatomic molecules have two final channels following triple ionization ($X^{2+}+Y^{+}$ or $X^{+}+Y^{2+}$). Nitric monoxide, NO, is discussed in this study, and we show that both the $N^{2+}+O^{+}$ and $N^{+}+O^{2+}$ channels are predominately formed nonvertically. Furthermore, two possible intermediate $N^{+}+O^{+}$ states exist for further dissociative triple ionization, and our data allow us to identify the intermediate state as a slowly dissociating $N^{+}+O^{+}$ channel. Finally, we show that both the $N^{2+}+O^{+}$ and $N^{+}+O^{2+}$ channels are formed at nearly the same internuclear separation that is much smaller than the critical internuclear distance for a diatomic molecule like NO. This indicates that dissociative ionization of high charge states can occur as a molecule steadily expands from its equilibrium separation rather than always at the critical internuclear distance.

The laser used in our 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 1.1 mJ/pulse at a 1 kHz repetition rate with the central wavelength at 800 nm. A thin lens is used to focus the laser 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 provides an ultrahigh resolution of 100 ps of the flight time. The field of the linearly polarized light is 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 species are essential in order to compare different channels. Using a technique described in Ref. [10], 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(a) shows TOF mass spectra across the delay range corresponding to the N^{+}, N^{2+}, O^{+}, O^{2+}, and NO^{2+} ions from ionization and dissociation of NO with linearly polarized light at an intensity of 5×10^{14} W/cm^2. Ions from different dissociation channels will arrive at the detector at a different time due to different charge/mass ratios and/or kinetic energy. Therefore, different dissociation channels can be distinguished from each other in the TOF mass spectrum. The dissociating ion pairs normally show symmetry in flight time around a zero-kinetic-energy peak representing initial

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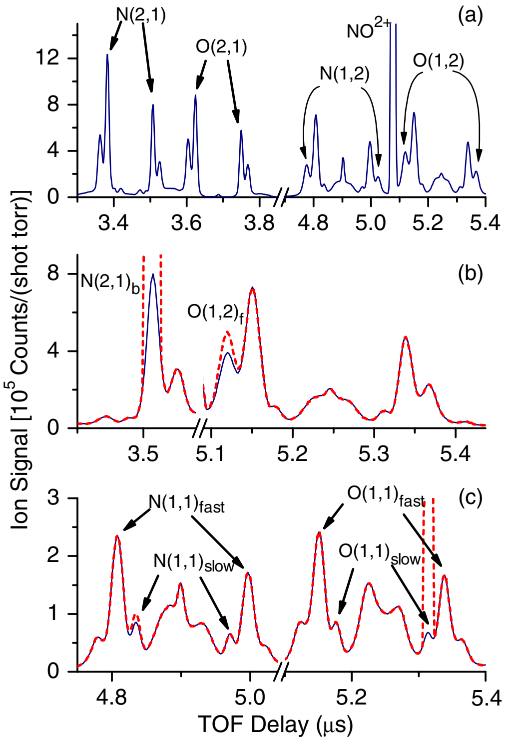

FIG. 1. (Color online) (a) TOF mass spectra of N^+, N^{2+}, O^+, and O^{2+} ions from ionization and dissociation of NO using linearly polarized light at an intensity of 5×10^{14} W/cm^2. (b) Ion-ion correlation spectrum for the $N^{2+}+O^+$ channel. The solid line is the spectrum averaged from all the laser shots, while the dashed line shows data averaged from only the laser shots containing a backward N^{2+} ion. $N(2,1)_b$ and $O(1,2)_f$ represent the backward N^{2+} and forward O^+ peaks, respectively, from the $N^{2+}+O^+$ channel. (c) Ion-ion correlation spectrum for the $(N^++O^+)_{slow}$ channel. The solid line is the spectrum averaged from all the laser shots, while the dashed line shows data averaged from only the laser shots containing a backward slow O^+ ion.

velocities either toward (forward ions) or away (backward ions) from the microchannel plate detector at the end of the TOF drift tube. To identify different dissociation channels, an ion-ion correlation technique is used [10]. For example, in Fig. 1(b), the solid line is the spectrum of the backward N^{2+} peak and all the O^+ peaks with data averaged from all the laser shots. We also average the data from only those laser shots containing the backward N^{2+} ion shown with the dashed line (within the range of the truncated dashed curves). If N^{2+} had no correlation with any O^+ peaks, the dashed line would represent an average of randomly selected data and would not affect the spectrum. However, if a correlation exists between the N^{2+} and an O^+ peak, the dashed line will show a difference from the solid line reflecting this correlation. As shown in Fig. 1(b), the majority of the spectrum remains unchanged on the O^+ side, but one peak clearly stands out and this O^+ peak must come from the same parent molecular ion as the trigger N^{2+} peak, i.e., $NO^{3+}\rightarrow N^{2+}+O^+$. Using this technique, we can identify all the dissociating ions from triply ionized NO. Note that throughout this paper we will label N^{2+} and O^+ form $N^{2+}+O^+$ as $N(2,1)$ and $O(1,2)$. Since $N(2,1)$ and $O(1,2)$ are correlated, we will only discuss one of the two ions. We choose to use $N(2,1)$ to represent the $N^{2+}+O^+$ channel because the $N(2,1)$ peak is cleaner in its surrounding TOF background [see Figs. 1(a) and 1(b)]. Similarly, N^+ and O^{2+} form N^++O^{2+} are labeled as $N(1,2)$ and $O(2,1)$, and $O(2,1)$ will be used to represent the N^++O^{2+} channel. Furthermore, we have also performed the ion-ion correlation measurements on double-ionization-induced N^++O^+ dissociation channels. As seen in Fig. 1(c), we notice that there are two pairs of N^++O^+ channels with different kinetic energy releases. We will label N^+ and O^+ from the slow dissociation channel as $N(1,1)_{slow}$ and $O(1,1)_{slow}$, while $N(1,1)_{fast}$ and $O(1,1)_{fast}$ represent the fast N^+ and O^+ fragments from the N^++O^+ channel. Here, we choose to study $N(1,1)_{fast}$ and $N(1,1)_{slow}$ to represent the fast and slow dissociation N^++O^+ channels, respectively. The total kinetic energy release of a dissociation channel is calculated by summing the kinetic energy carried by each ion fragment. At an intensity of 5×10^{14} W/cm^2, the total kinetic energy release is determined to be 13.9 eV for the N^++O^{2+} channel and 13.7 eV for the $N^{2+}+O^+$ channel.

The two N^++O^+ channels with different kinetic energy releases can be understood by considering the detailed electronic structure of diatomic molecule NO. The outer electronic configuration for the ground state of molecule NO $X\,^2\Pi$ is $KK(1\pi)^4(5\sigma)^2(2\pi)^1$, where $(2\pi)^1$ is an antibonding orbital while $(1\pi)^4$ is a strongly bonding orbital [11]. The removal of two strongly bonding 1π electrons will lead to a dissociation N^++O^+ channel with a relatively large kinetic energy release due to the strong Coulomb repulsion, and previous studies have shown that this will yield the fast $N(1,1)_{fast}$ channel [12]. There have been some controversies on the bonding nature of the $(5\sigma)^2$ orbital: some work assigns the $(5\sigma)^2$ orbital as antibonding [11] while some assign it as bonding [13,14]. Previous studies showed that the equilibrium separation r_e for NO^+ in the $A\,^1\Pi\ (5\sigma^{-1})$ state will increase slightly compared to the neutral NO molecule when one of the 5σ electrons is removed, and this indicates that the $(5\sigma)^2$ orbital has some weakly bonding nature [15]. Thus, there is also some probability for NO^{2+} to dissociate when the two 5σ electrons are removed, and this leads to the slow N^++O^+ channel [16]. Studies using photoelectron spectroscopy [17] and electron-ion coincidence techniques [18] may help one gain further understanding of the fast and slow N^++O^+ channels. However, these studies are relatively unimportant for our further discussions in this paper.

Figure 2 shows the intensity-dependent ionization yields of $N(2,1)$, $O(2,1)$, $N(1,1)_{fast}$, and $N(1,1)_{slow}$ channels with linearly polarized light. As we can see from Fig. 2, an ion yield of $N(1,1)_{slow}$ is higher than $N(1,1)_{fast}$ at a lower intensity range, indicating $N(1,1)_{slow}$ is easier to reach at low intensities compared to $N(1,1)_{fast}$. This is reasonable since it is easier to remove a pair of 5σ electrons than a pair of 1π electrons in NO. Also from Fig. 2, we can see that $N(2,1)$ and $O(2,1)$ have almost the same intensity dependence, indicating these two channels may come from the same precursor. If these two triple-ionization-induced dissociation channels are formed vertically at the equilibrium internuclear separation of molecule NO, the strong Coulomb explosion should yield a kinetic energy release of ~25.3 eV, and this

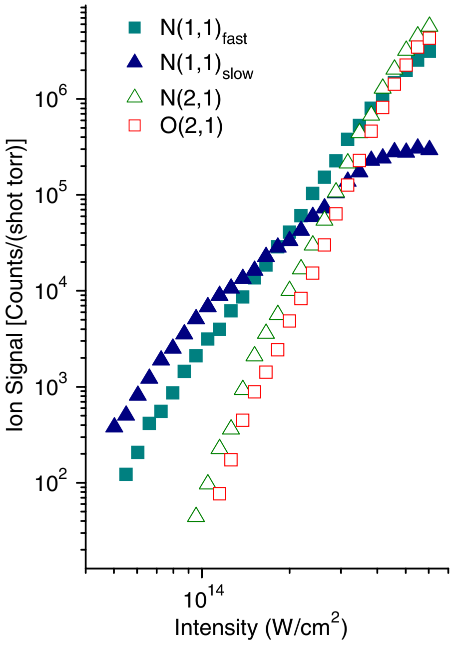

FIG. 2. (Color online) Ionization yields of $N(1,1)_{fast}$, $N(1,1)_{slow}$, $N(2,1)$, and $O(2,1)$ using linearly polarized light.

value is about twice as high as the total kinetic energy release of $N(2,1)$ and $O(2,1)$ observed in our experiment. Therefore, the $N(2,1)$ and $O(2,1)$ channels should be reached nonvertically through an intermediate $N^{+}+O^{+}$ state by ionizing the third electron at a greater internuclear separation as the dissociating N^{+} and O^{+} ions separate from each other. As we can see from Fig. 2, despite the fact that the energy levels for $N(2,1)$ and $O(2,1)$ are much higher than the $N^{+}+O^{+}$ channel, the ion yields of $N(2,1)$ and $O(2,1)$ surpass that of $N(1,1)_{slow}$ at the higher intensity range. This indicates that $N(2,1)$ and $O(2,1)$ start to deplete $N(1,1)_{slow}$ at higher intensities, suggesting that $N(1,1)_{slow}$ is the intermediate state of both $N(2,1)$ and $O(2,1)$.

The question of whether $N(2,1)$ and $O(2,1)$ proceed through $N(1,1)_{slow}$ can be answered experimentally by utilizing a well-established technique [7,10,19] from the study of sequential versus nonsequential ionization by analyzing the intensity dependence of the ion ratio curves, where the intensity dependence can reflect whether double ionization needs to proceed through single ionization. In our case, we will analyze the intensity-dependent ratio curves of $N(2,1)/N(1,1)_{slow}$, $O(2,1)/N(1,1)_{slow}$, $N(2,1)/N(1,1)_{fast}$, and $O(2,1)/N(1,1)_{fast}$. Taking $N(2,1)/N(1,1)_{slow}$ as an example, if $N(2,1)$ is produced through the intermediate state $N(1,1)_{slow}$, the ratio $N(2,1)/N(1,1)_{slow}$ will have a strong intensity dependence [9]. However, if this ratio depends only weakly on intensity, it shows that the precursor to $N(2,1)$ is not $N(1,1)_{slow}$. Intensity-dependent ratio curves are plotted in Fig. 3 for $N(2,1)/N(1,1)_{slow}$, $O(2,1)/N(1,1)_{slow}$, $N(2,1)/N(1,1)_{fast}$, and $O(2,1)/N(1,1)_{fast}$ with linearly polarized light. A strong intensity dependence is seen in the ratio curves of $N(2,1)/N(1,1)_{slow}$ and $O(2,1)/N(1,1)_{slow}$, while the ratio curves of $N(2,1)/N(1,1)_{fast}$ and $O(2,1)/N(1,1)_{fast}$ show a weaker intensity dependence. This

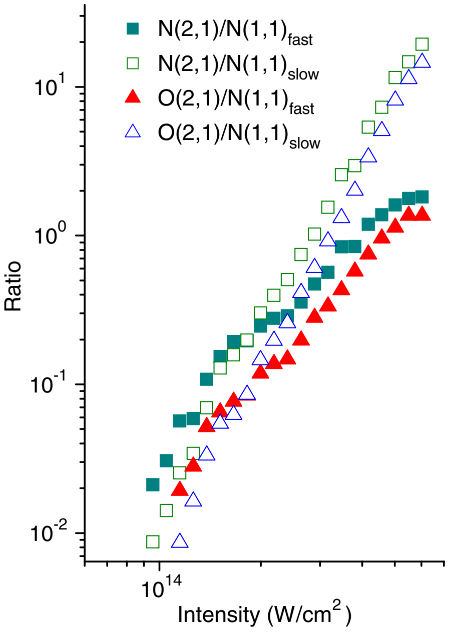

FIG. 3. (Color online) Intensity-dependent ratio curves for $N(2,1)/N(1,1)_{fast}$, $N(2,1)/N(1,1)_{slow}$, $O(2,1)/N(1,1)_{fast}$, and $O(2,1)/N(1,1)_{slow}$ using linearly polarized light.

indicates that both $N(2,1)$ and $O(2,1)$ are predominately produced through the intermediate $N(1,1)_{slow}$ state rather than $N(1,1)_{fast}$, in agreement with our observation that $N(1,1)_{slow}$ but not $N(1,1)_{fast}$ is depleted by $N(2,1)$ and $O(2,1)$ at higher intensities. It is indeed reasonable since $N(1,1)_{slow}$ is easier to reach than $N(1,1)_{fast}$ and can be formed at an earlier time during the rising edge of our pulse, allowing a higher probability for a nonvertical transition to reach the triple-ionization-induced dissociation states, $N(2,1)$ and $O(2,1)$.

In our experiment, the internuclear separation where $N(2,1)$ and $O(2,1)$ are formed can be deduced from their corresponding kinetic energy release. The energy threshold for $N(2,1)$ and $O(2,1)$ is determined to be 64.3 and 69.8 eV above the ground state of the neutral molecule NO. Since both $N(2,1)$ and $O(2,1)$ are formed from the same intermediate $N(1,1)_{slow}$ state, it should be harder to access $O(2,1)$ than $N(2,1)$ since $O(2,1)$ lies higher in energy. Therefore, it would require a higher field strength to ionize a third electron to reach $O(2,1)$ than $N(2,1)$ from $N(1,1)_{slow}$, i.e., $O(2,1)$ should be produced at a later time of the rising edge of our laser pulse than $N(2,1)$. This suggests that $N(2,1)$ and $O(2,1)$ are formed at different internuclear separations as N^{+} and O^{+} are separating from each other. However, our data show that $N(2,1)$ and $O(2,1)$ have nearly identical kinetic energy release (13.7 versus 13.9 eV), and this indicates that ionization of the third electron to form $N(2,1)$ and $O(2,1)$ occurs at nearly the same internuclear separation if we assume both $N(2,1)$ and $O(2,1)$ dissociation curves are Coulombic [both $N(2,1)$ and $O(2,1)$ channels are produced through the same intermediate $N(1,1)_{slow}$ channel that has a kinetic energy release of 4.1 eV]. Based on the Coulomb explosion model [4,20], we estimate that ionization of the third electron to reach N(2,1) and O(2,1) through $N(1,1)_{slow}$ occurs at an internuclear separation of about 1.5 Å, which is much smaller than the critical internuclear distance for a diatomic molecule like NO (~4 Å) [20]. Therefore, in contrast to the common belief that high charge dissociative ionization in molecules is predominately formed at a critical internuclear distance R_c [21,22], triple ionization of NO in our experiment occurs much before R_c; similar effects have also been observed in other diatomic molecules, such as N_2 [23].

In summary, we performed a study on the dynamics of triple-ionization-induced dissociation in a heteronuclear diatomic molecule NO. Compared to homonuclear diatomic molecules, NO shows a greater complexity in its final states following triple ionization. By utilizing a well-established technique from the study of sequential versus nonsequential ionization, our study shows that both the N^{2+}+O^{+} and N^{+}+O^{2+} channels are predominately formed nonvertically through a relatively slowly dissociating N^{+}+O^{+} state. Finally, we show that both the N^{2+}+O^{+} and N^{+}+O^{2+} channels are formed at nearly the same internuclear separation, which is much smaller than the critical internuclear distance. This indicates that dissociative ionization of high charge states in a molecule can occur as a molecule steadily expands from its equilibrium separation rather than always at the critical internuclear distance.

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