Vertical and nonvertical transitions in triple-ionization-induced dissociation of diatomic molecules

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In this paper, we study triple-ionization-induced dissociation in N_2 and O_2 for laser polarization aligning either parallel or perpendicular along the molecular axis. For the first time, we demonstrate that vertical or nonvertical transition can be turned on and off by simply switching the laser polarization between being perpendicular and parallel to the molecular axis. We also show that the dependence of kinetic energy release on intensity can be used to distinguish vertical from nonvertical transition in triple-ionization-induced dissociation.

The study of dissociation dynamics following multielectron ionization of molecules has attracted much attention recently in strong field physics [1–9]. In the past, two mechanisms have been suggested to account for the dissociation dynamics following multielectron ionization of a molecule, vertical transition and nonvertical transition [1–5]. Taking a triply ionized homonuclear 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 relatively high kinetic energy release (KER) due to a strong Coulomb explosion from the equilibrium internuclear separation [1,2]. In the nonvertical transition, X_2 can be first doubly ionized leading to X_2^{2+}, and X_2^{2+} will then start to dissociate to two X^+ ions. If the laser intensity continually rises while X_2^{2+} dissociates, a third electron may be liberated leading to the $X^{2+}+X^+$ dissociation channel [3–5]. This nonvertical stepwise process will lead to a smaller KER. Previous studies show that both vertical and nonvertical transitions can occur in triple-ionization-induced dissociation channels, and the detailed dynamics will depend on the laser wavelength, pulse width, and the type of molecules [1–5]. In general, a shorter laser pulse at shorter wavelength will more likely lead to the vertical transition, while the nonvertical transition is more likely seen using a longer pulse at longer wavelength. Recently, we performed a study on triple-ionization-induced dissociation in diatomic molecules N_2 and O_2 by applying laser polarization along the molecular axis [10]. Our study show that, for the parallel ionization, $O^{2+}+O^+$ is predominately produced nonvertically through the intermediate O^++O^+ channel, while $N^{2+}+N^+$ is formed vertically at the lower intensity range but nonvertically at higher intensities.

One of the most unique effects for molecular ionization is that ionization process can be significantly different when the angle between the external laser field and the molecular axis varies. In other words, parallel ionization (the laser field parallel to the molecular axis) can be quite different from perpendicular ionization (the laser field perpendicular to the molecular axis) [11,12]. In this paper, we investigate if triple ionization parallel or perpendicularly has any effects on the final dissociation dynamics (vertically or nonvertically) in molecules. In contrast to our previous results with only parallel triple ionization in N_2 and O_2 [10], we find that both the $N^{2+}+N^+$ and $O^{2+}+O^+$ channels are predominately produced vertically for perpendicular ionization. To identify the origin of the $N^{2+}+N^+$ and $O^{2+}+O^+$ channels following both parallel and perpendicular ionization, intensity dependent KER for both channels is examined.

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, and a zero-order half wave plate is used before the focusing lens to control the polarization of the laser light to be either parallel or perpendicular to the time of flight (TOF) axis. 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. The details of our experimental setup have been described elsewhere [13]. In brief, a standard TOF mass spectrometer is used for ion collection and detection. The TOF voltage plates for extracting and accelerating ions each has only a 1 mm pinhole opening to allow ions to pass through. At the end of the TOF, ions are detected with a microchannel plate (MCP) 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 in the experiment provides an ultrahigh resolution of 100 ps of flight time, which allows us to study molecular ionization and dissociation dynamics in a greater detail. High-precision ionization yield measurements of different species are essential in order to compare different channels. Using a technique described in Ref. [12], we are able to accurately determine the flight time and width of a certain species and isolate it from contamination from adjacent peaks.

In our experiment, molecules in the target region are randomly oriented. However, since dissociation ions following

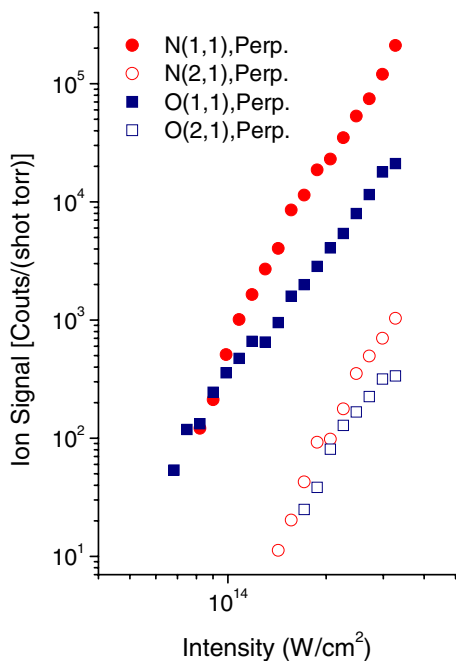*Corresponding author. Electronic address: guo@optics.rochester.edu

FIG. 1. (Color online) Ionization yields of N(1,1), N(2,1), O(1,1) and O(2,1) channels for perpendicular ionization.

FIG. 2. (Color online) Ratio curves of N(2,1)/N(1,1) and O(2,1)/O(1,1) for both parallel and perpendicular ionizations.

triple ionization have relatively large KER, the two 1 mm pinholes in our TOF spectrometer essentially allow us to selectively collect ion signals only from the molecules that initially orient and dissociate along the TOF axis. Indeed, molecules dissociating along the TOF axis can be readily distinguished from the molecules perpendicular to the TOF axis: for the molecules initially oriented parallel to the TOF axis, dissociation channels all have a double peak structure corresponding to the ions with initial velocity towards and away from the MCP detector at the end of the TOF drift tube, while for the molecules initially oriented perpendicular to the TOF axis, the dissociation ions, if they could pass through the pinholes, will have a near-zero kinetic energy on the TOF spectra and will be recorded in the central region between the two ion peaks resulting from the parallel oriented molecules [13]. In our experiment, we will confine our attention to study molecules that initially orient and dissociate along the TOF axis. Therefore, the parallel ionization in our work refers to the ionization when our laser polarization is also parallel to the TOF axis, while the perpendicular ionization refers to the ionization when our laser polarization is perpendicular to the TOF axis. An ion-ion correlation technique similar to that used in Ref. [12] is also used to verify the identification of different dissociation channels. Note, throughout this paper we will label N^+ and N^{2+} from the $N^+ + N^{2+}$ channel as N(1,2) and N(2,1). Since N(1,2) and N(2,1) are from the same triply ionized parent ion, we will only discuss one of these two species. We choose to study N(2,1) in this paper 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.

As proposed in Ref. [10], the question of whether the triple-ionization-induced dissociation channel is produced
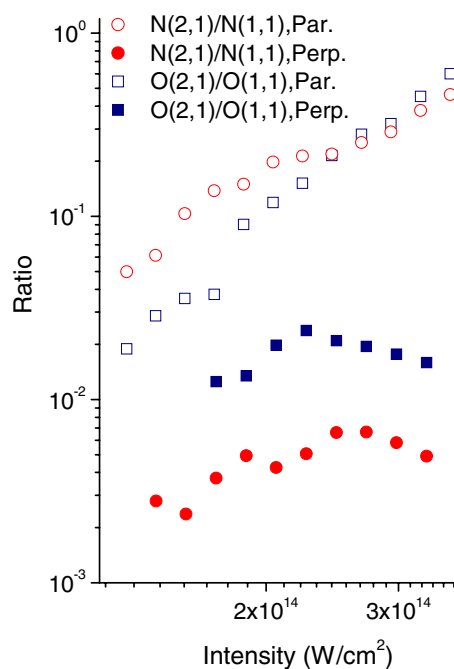
vertically or nonvertically can be answered experimentally by utilizing a well-established technique [8,12,14,15] from the study of sequential versus nonsequential ionization by analyzing the intensity dependence of ion yield ratio curves, where the intensity dependence can reflect if triple ionization needs to proceed through a lower charge state. 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 dissociation $N^+ + N^+$ and $O^+ + O^+$ channel, respectively. Taking O(2,1)/O(1,1) as an example, if O(2,1) is produced nonvertically through the intermediate state O(1,1), the ratio O(2,1)/O(1,1) will have a strong intensity dependence. However, if this ratio depends only weakly on intensity, it shows that O(2,1) does not need to proceed through the dissociating O(1,1) state. Figure 1 shows the intensity dependent ionization yields of N(1,1), N(2,1), O(1,1), and O(2,1) channels for perpendicular ionization. The corresponding intensity dependent ratio curves of N(2,1)/N(1,1) and O(2,1)/O(1,1) are shown in Fig. 2. For comparison, the ratio curves for parallel ionization are also plotted in Fig. 2. Vertical and nonvertical transitions have been previously studied in details for N(2,1) and O(2,1) for parallel ionization only [10] and as reflected in Fig. 2, O(2,1) is predominately produced nonvertically through the intermediate $O^+ + O^+$ channel, while N(2,1) is also formed nonvertically at higher intensities although there exists some vertical component at the lower intensity range. In contrast, the ratio curves of N(2,1)/N(1,1) and O(2,1)/O(1,1) show much weaker dependency on intensity for perpendicular ionization than parallel ionization, indicating that vertical transitions dominate the formation of both O(2,1) and N(2,1) for perpendicular ionization. We would like to note that this is the first time that we demonstrate that vertical or nonvertical transition can be turned on and off by simply switching the
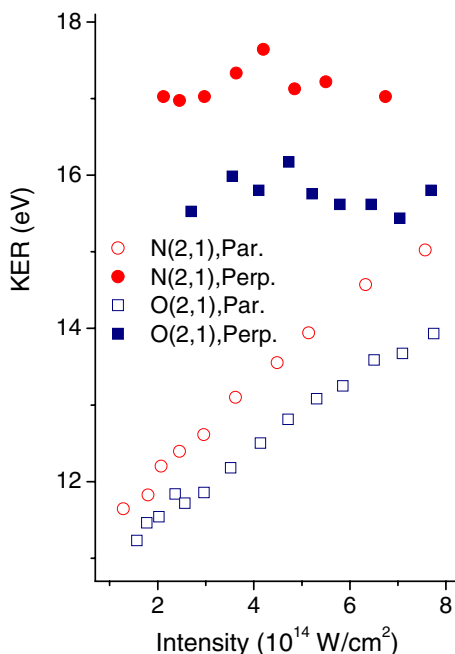
FIG. 3. (Color online) Intensity dependent KER of the N(2,1) and O(2,1) channels for both parallel and perpendicular ionizations.
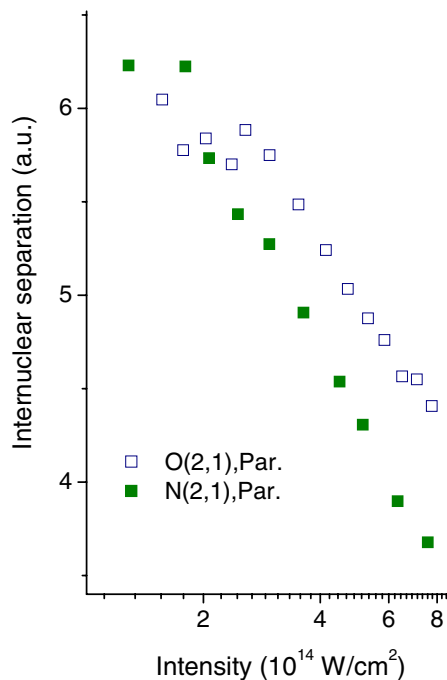

FIG. 4. (Color online) Calculated internuclear separation where the N(2,1) and O(2,1) channels are formed from the dissociating doubly charged state as a function of laser intensity for parallel ionization.

laser polarization between perpendicular ionization and parallel ionization. This observation is reasonable because, for parallel ionization, a two-step enhanced triple ionization may occur when the third electron is removed at a critical internuclear distance as the two X^+ ion cores separate from each other following the removal of the first two electrons. The enhanced ionization at a critical internuclear separation has been studied extensively before [3–5,11], including mechanisms such as charge-resonance-enhanced ionization [16]. One the other hand, since the enhanced ionization at the critical internuclear distance does not exist for perpendicular ionization [11], there may be a greater possibility for triple electron ionization occurs simultaneously for perpendicular ionization.

To identify the origin of the dissociation channels following different light polarizations, we study KER of various channels through TOF mass spectrum measurements. The ultrahigh time resolution of our TOF measurements allows us to accurately determine KER from different dissociation channels. In Fig. 3, KER of the N(2,1) and O(2,1) channels are plotted as a function of intensity for both parallel and perpendicular ionizations. We can see that KER of both N(2,1) and O(2,1) show very different intensity dependency between parallel and perpendicular ionization, indicating that N(2,1) and O(2,1) must come from different processes following parallel ionization versus perpendicular ionization. The KER curves of both O(2,1) and N(2,1) are strongly dependent on intensity for parallel ionization, while the KER curves are almost constant as intensity varies for perpendicular ionization. We believe that the stronger intensity dependent KER is an indication of a step-wise ionization process (nonvertical transition) for the following reason. For triple ionization following nonvertical transition in a diatomic molecule, after the first two electrons are removed, two atomic

cores will start to separate from each other due to Coulomb repulsion. If the pulse intensity continuously increases and becomes strong enough to remove the third electron, triple ionization will occur [3–5]. Therefore, triple ionization will occur at an earlier time and shorter internuclear separation as the pulse peak-intensity increases. Based on the simple Coulomb explosion model [4,17], KER of the dissociation ions is inversely proportional to the internuclear separation where they are produced. Therefore, for a step-wise nonvertical ionization, KER of the dissociation ions will increase with intensity. However, for vertical ionization, the dependence of KER on intensity should be small, if at all, since all the electrons are removed almost simultaneously. Therefore, our experimental results from the intensity dependent KER also agree with the ion yield ratio curve analysis in Fig. 2. Both data show that both O(2,1) and N(2,1) have significant nonvertical component following parallel ionization, while both channels are predominately produced vertically following perpendicular ionization.

Based on the measured KER, the internuclear separation where N(2,1) and O(2,1) are formed nonvertically through N(1,1) and O(1,1) can be estimated according to the Coulomb model, $r(\text{Å}) = 14.4(2 \times 1 - 1 \times 1)/\Delta U(\text{eV})$ [4], where ΔU is the KER difference between the triple- and double-ionization-induced dissociation channels. The internuclear separation to form N(2,1) and O(2,1) through N(1,1) and O(1,1) are plotted in Fig. 4 as a function of laser intensity. We can see that the third electron ionization occurs at a shorter internuclear separation (ranging from 6.2 to 3.6 a.u.) as the laser intensity increases. According to the Coulomb model [4], the values of KER for vertical transitions at the equilibrium internuclear separations are about 26 eV and

24 eV, respectively, for N(2,1) and O(2,1). However, the measured values in our experiment for perpendicular ionization, ∼17.2 eV for N(2,1) and ∼15.7 eV for O(2,1), are significantly smaller than the expected values for vertical transitions. Since our experimental results have consistently show that N(2,1) and O(2,1) are reached vertically following perpendicular ionization, the final atomic ions must be in excited states for N(2,1) and O(2,1) following perpendicular ionization in our experiment. In fact, there have been a number of recent studies indicating that molecular ions often residing in their excited states following ultrashort pulse excitation [8,10,18,19], and this is consistent with what we see here in the N(2,1) and O(2,1) channels for perpendicular ionization. We also perform semi-classical numerical simulations by only examining the process of the third electron ionization from X_2^{2+}. Our simulations are carried out by treating electrons as waves and atomic cores as classical particles [20]. The motion of the nuclei is limited in one-dimenional (1D), and the electron wave function is limited in two-dimensional (2D). An external field is added along the internuclear axis to simulate parallel ionization. Although these much simplified calculations cannot directly compare to our experimental conditions, the simulation results also show that there exists a strong intensity dependence for KER

in nonvertically triple-ionization-induced dissociation, which is consistent with our experimental results for parallel ionization in both O(2,1) and N(2,1).

In summary, we study triple-ionization-induced dissociation in N_2 and O_2 for laser polarization aligning either parallel or perpendicular along the molecular axis. For the first time, we demonstrate that vertical or nonvertical transition can be turned on and off by simply switching the laser polarization between perpendicular ionization and parallel ionization. We also show that the dependence of KER on intensity can be used to distinguish nonvertical from vertical transition in triple-ionization-induced dissociation, i.e., a stronger intensity dependence of KER corresponds to a higher probability for nonvertical transition, while a weaker intensity dependence of KER corresponds to a higher probability for vertical transition. The results in this paper allow us to gain a better understanding on the possibility to control the pathway of molecular dissociative ionization following triple ionization, as we have already studied previously for lower charge states [21,22].

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