PHYSICAL REVIEW A **75**, 043402 (2007)

Polarization effects on nonsequential double ionization of molecular fragments in strong laser fields

Jian Wu, Heping Zeng, and Chunlei Guo*
The Institute of Optics, University of Rochester, Rochester, New York 14627, USA

(Received 18 August 2006; published 11 April 2007)

In this paper, we study nonsequential double ionization in various molecular fragments for laser polarization aligning either parallel or perpendicular to the molecular axis. In the diatomic molecule O_2, we find that nonsequential double ionization can be turned on and off when we simply switch the laser polarization between perpendicular and parallel ionization. Furthermore, we find that the dependence of kinetic energy release on intensity can be used to distinguish sequential versus nonsequential ionization in molecules. The results in this paper allow us to gain better understanding of the role of nonsequential ionization in molecular dissociative ionization.

DOI: 10.1103/PhysRevA.75.043402 PACS number(s): 33.80.Rv, 33.80.Gj, 42.50.Hz

Recently, phenomena related to multielectron effects have drawn more and more attention in strong-field atomic and molecular physics. Among these phenomena, nonsequential double ionization (NSDI) is one of the most interesting and challenging problems. NSDI normally refers to an enhancement in double-ionization yields compared to calculations based on sequential processes [1–15]. Originally, the study of NSDI was mainly carried out using rare-gas atoms which all have similar closed-shell electronic structures [1–8]. NSDI has been seen in all the rare-gas atoms to a similar degree [1–8]. More recently, the studies of NSDI have been extended to various diatomic molecules, and the results show that the detailed electronic structures play a key role in influencing NSDI rates [9–15]. Furthermore, molecules may also behave differently in NSDI from what we have learned from rare-gas atoms. For example, in linearly polarized light, ${N_2}^{2+}$ shows a significantly higher NSDI rate than ${O_2}^{2+}$ due to the fact that N_2 has a closed-shell electronic structure with the outermost two electrons responsible for double ionization being in the same orbital, while O_2 has an open-shell structure with the outermost two electrons being in two different but degenerate orbitals [9]. More interestingly, we also observed a high NSDI rate in NO and O_2 molecules with circular polarization [11,12], and this observation deviates significantly from the ellipticity effects established from the study of rare-gas atoms [1–8].

One of the most interesting effects for molecular ionization is that ionization processes 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) [10,15–18]. In this paper, we investigate the different effects of parallel ionization versus perpendicular ionization on NSDI. We will again study the two benchmark molecules N_2 and O_2, which have helped us gain significantly more understanding on strong-field phenomena [9–13,15,19–21]. To better resolve the difference between parallel and perpendicular ionization, dissociation channels are used in our experiment, including $N^{+}+N^{+}$ [labeled as N(1,1) throughout the paper] and $O^{+}+O^{+}$ [labeled as O(1,1) throughout the paper]. Our experimental results show that a high NSDI rate exists in both the N(1,1) and O(1,1) channels for perpendicular ionization, even though NSDI nearly vanishes in O(1,1) for parallel ionization. To identify the origin of the N(1,1) and O(1,1) channels following parallel and perpendicular ionization, intensity-dependent kinetic energy release (KER) for both N(1,1) and O(1,1) is examined under different conditions.

The laser used in our experiment is an amplified Ti:sapphire system. 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 (*p* polarization) or perpendicular (*s* polarization) 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 details of our experimental setup have been described elsewhere [22]. In brief, a standard TOF mass spectrometer is used for ion collection and detection. The TOF voltage plates for extracting and accelerating ions each have only a 1 mm pinhole opening to allow ions to pass through. The time digitizer used in the experiment provides an ultrahigh resolution of 100 ps of flight time.

In our experiment, molecules in the target region are randomly oriented. However, since dissociation ions following double 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 that initially orient and dissociate along the TOF axis can be readily distinguished from the molecules perpendicular to the TOF axis since they will be recorded at a different time delay in TOF spectra due to their different KER component along the TOF axis [22]. Because of the small pinholes, the molecular fragments we collect in our experiment are those that initially orient and dissociate along

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

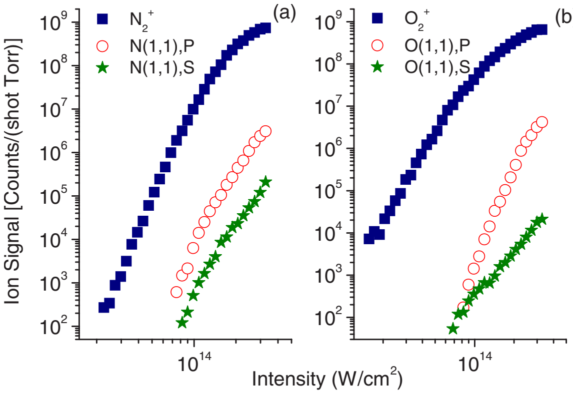

FIG. 1. (Color online) Ionization yields of (a) N_2^+ and N^+ from the N(1,1) channel and (b) O_2^+ and O^+ from the O(1,1) channel with both *p* and *s* polarizations.

the TOF axis. Therefore, the parallel ionization in our paper refers to the ionization when our laser polarization is also parallel to the TOF axis (*p* polarization), while the perpendicular ionization refers to the ionization when our laser polarization is perpendicular to the TOF axis (*s* polarization). An ion-ion correlation technique similar to that used in Ref. [10] is also used to verify the identification of different dissociation channels.

Figure 1 shows the intensity-dependent ionization yields of N_2^+, O_2^+, N(1,1), and O(1,1) channels with *p*-polarized (parallel ionization) and *s*-polarized (perpendicular ionization) light. In our experiment, laser polarization has no effect on the nondissociation ionic channels and thus the ion yields of N_2^+ and O_2^+ in Fig. 1 are taken using only *p*-polarized light. For the dissociation channels, however, the signal strength of N(1,1) and O(1,1) decreases significantly when the light polarization is changed from *p* to *s*, since it is much harder to remove an electron when the laser field orients perpendicular to the molecular axis than parallel to the molecular axis [10,16]. When we further examine the intensity dependence of the ion yields, the N(1,1) ion yields for *p* and *s* polarizations show similar intensity dependence; however, the O(1,1) ion yields show very different intensity dependence between the *p* and *s* polarizations. This indicates that N(1,1) is most likely formed through the same ionization process between the two polarizations, but the ionization process to reach O(1,1) may be different for parallel ionization compared to perpendicular ionization.

In general, double ionization can proceed through two possible processes, i.e., sequential and nonsequential ionization. Experimentally, sequential double ionization can be easily distinguished from NSDI by utilizing a well-established technique based on the intensity dependence of ratio X^{2+}/X^+, where X^+ and X^{2+} are the yields for single and double ionization of the same atom or molecule X [3,9–12]. Nonsequential dynamics is most fundamentally related to this ratio: if X^{2+} is produced through a sequential process, X^+ will be the intermediate species and the ratio X^{2+}/X^+ will reflect just the ionization rate from X^+ to X^{2+} that will have a strong intensity dependence. However, if this ratio is only weakly dependent on intensity, it shows that the precursor to X^{2+} is not X^+, and the ionization will involve the nonsequential process. In Fig. 2, ratio curves of $N(1,1)/N_2^+$ and $O(1,1)/O_2^+$ are plotted for both *p* and *s* polarizations. For parallel ionization with *p*-polarized light, $N(1,1)/N_2^+$ shows a clearly weaker intensity dependence than $O(1,1)/O_2^+$, indicating that N(1,1) has a much higher NSDI rate than O(1,1). This observation is in agreement with a previous study [10], and the difference can be understood by considering the electronic structures of N_2 and O_2 as follows. The ground-state electronic configurations of N_2 and O_2 are $KK(1\pi_u)^4(3\sigma_g)^2$ and $KK(1\pi_u)^4(1\pi_g)^2$, respectively [23]. The formation of N(1,1) involves the removal of two bonding electrons from the same closed-shell orbital $(3\sigma_g)^2$, while O(1,1) is formed by removing one bonding $1\pi_u$ and one antibonding $1\pi_g$ electron [10]. According to the properties established in studying metastable N_2^{2+} and O_2^{2+}, we expect a higher NSDI rate when the two removed electrons are in the same orbital and a lower NSDI rate when the two removed electrons are in different orbitals [9–12]. Therefore, we see a higher NSDI rate in N(1,1) but a much lower NSDI rate in O(1,1). However, when the light polarization is switched from *p* to *s*, both the ratio curves of $N(1,1)/N_2^+$ and $O(1,1)/O_2^+$ show weak intensity dependence, as seen in Fig. 2. This indicates that a significant NSDI component exists in both N(1,1) and O(1,1) channels for perpendicular ionization. Thus we have demonstrated that NSDI can be turned on and off by simply switching the laser polarization between perpendicular and parallel ionization.

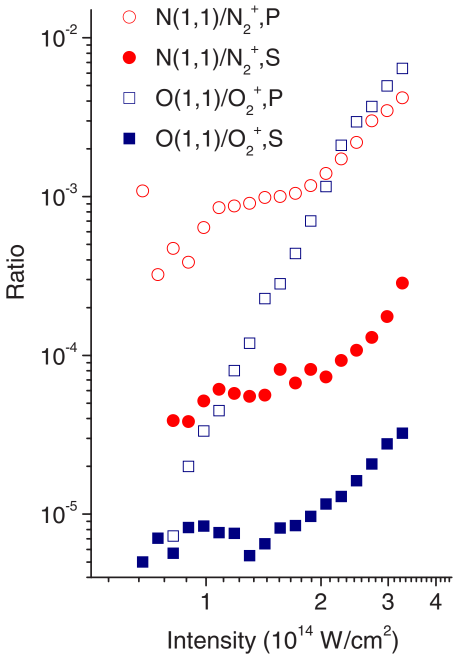

FIG. 2. (Color online) Ratio curves of $O(1,1)/O_2^+$ and $N(1,1)/N_2^+$ with both *p* and *s* polarizations.

To identify the origin of the dissociation channels following different light polarizations, we further study the KER of various channels through TOF mass spectrum measurements. The ultrahigh time resolution (100 ps) of our TOF measurements allows us to accurately determine the KER of different dissociation channels. In Fig. 3, KER of the N(1,1) and O(1,1) channels are plotted for both *p* and *s* polarizations as

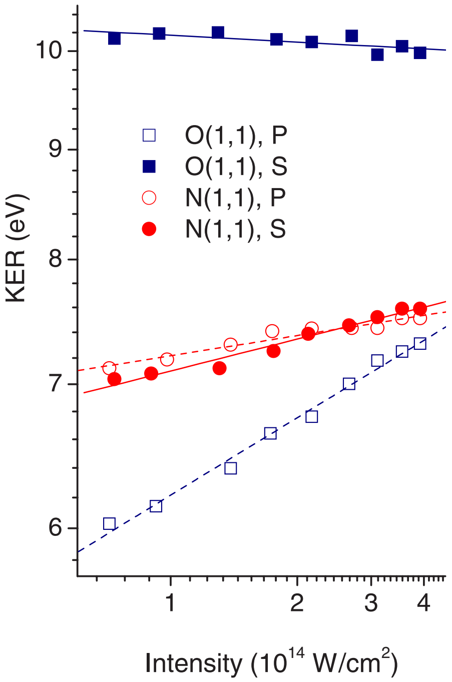

FIG. 3. (Color online) KER of the O(1,1) and N(1,1) channels as a function of intensity with both *p* and *s* polarizations. The intensity dependence of each ratio curve is fitted with a straight line, also shown in the figure.

a function of intensity. We note from Fig. 3 that KER for the O(1,1) channel is about 3 eV larger following ionization by *s* polarization than by *p* polarization. On the other hand, KER for the N(1,1) channel is similar between the parallel and perpendicular ionization. This indicates that N(1,1) is reached by a similar ionization process between *p* and *s* polarization. However, the ionization process that leads to O(1,1) must be significantly different between *p* and *s* polarization.

In order to understand the different KER of O(1,1) following ionization by *p*-polarized and *s*-polarized light, we again examine the detailed initial electronic structure of O_2. As we discussed above, the removal of one electron from the $(1\pi_g)^2$ antibonding orbital and another one from the inner bonding $(1\pi_u)^4$ orbital will lead to unstable O_2^{2+}, and this ionization pathway will yield the $O^+ + O^+$ channel following parallel ionization [10]. However, two electrons can also be removed from the same inner bonding $(1\pi_u)^4$ orbital. In this case, O_2^{2+} will certainly dissociate but with much higher KER. We believe that the high KER in O(1,1) from perpendicular ionization is the result of the removal of the two bonding $1\pi_u$ electrons. This also explains why we see a higher NSDI rate in O(1,1) for perpendicular than for parallel ionization (see the ratio curves in Fig. 2), since the removed two electrons are from the same closed-shell orbital for perpendicular ionization.

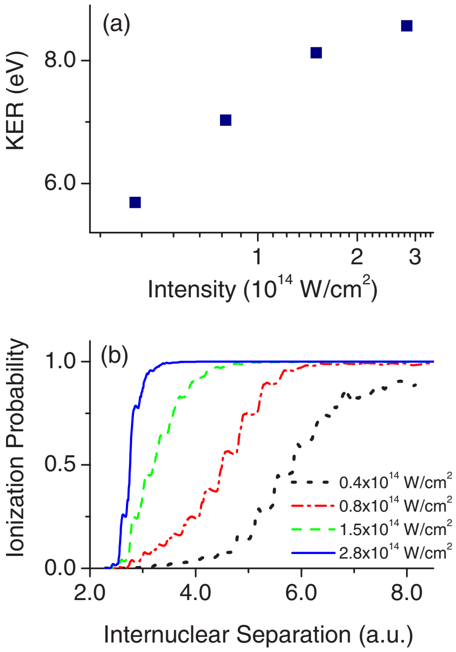

FIG. 4. (Color online) Calculated results of (a) intensity-dependent KER and (b) ionization probabilities as a function of internuclear distance for parallel ionization.

From Fig. 3, we can see that all the KER curves are weakly dependent on intensity except the O(1,1) channel following *p*-polarized parallel ionization. The intensity dependence of each ratio curve is fitted with a linear line and also shown in the figure. The fittings indicate that the slope of the KER curve for the parallel-ionization-induced O(1,1) channel is more than 2.4 times greater than the other KER slopes. This again indicates that O(1,1) following double ionization by *p*-polarized light must come from a different process than the other three dissociation channels. We believe that the more strongly intensity-dependent KER is an indication of a stepwise sequential ionization process for the following reason. For sequential double ionization in a diatomic molecule, after the first electron is removed, the two atomic cores may start to separate from each other. If the pulse intensity continuously increases and becomes strong enough to remove the second electron, double ionization will occur. Therefore, double ionization will occur at an earlier time and shorter internuclear separation as the pulse peak intensity increases. Based on the simple Coulomb explosion model [24,25], the KER of the dissociating ions is inversely proportional to the internuclear separation where they are produced. Therefore, for sequential ionization, the KER of the dissociating ions will increase with intensity. However, for NSDI, the dependence of the KER on intensity should be small, if any, since the two electrons are removed 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 O(1,1) following parallel ionization is a sequential process, while O(1,1) following perpendicular ionization and N(1,1) following both parallel and perpendicular ionization come from NSDI. The electron and ion momenta following double ionization in N_2 and O_2 have also been studied previously using the electron and ion momentum technique [13,15]. In our experiment, however, the KER is measured at a variety of intensities and our results show that the dependence of KER on intensity can be used to distinguish sequential versus nonsequential ionization in diatomic molecules.

In order to further verify that sequential ionization will result in a stronger intensity dependence of KER in dissociation channels, we perform semiclassical numerical calculations by treating electrons as waves and atomic cores as classical particles [26]. We only look at the sequential process here, and our simulation describes the ionization and dissociation processes when the second electron is removed from a singly ionized molecule. Therefore, our starting point is one electron shared by two atomic ion cores each with one positive charge. The initial internuclear separation is chosen to be 2.3 a.u., the equilibrium value for O_2. A ten-cycle trapezoidal pulse with central wavelength at 800 nm and polarization along the molecular axis is used in the calculations, and the pulse includes two-cycle linear turn-on and two-cycle linear turn-off [8,26]. At the end of the pulse, the KER of a dissociation channel is calculated by summing the kinetic energy carried by each core. As shown in Fig. 4(a), the simulation results show a strong intensity dependence in the final KER for the sequential process with parallel ionization, i.e., KER increases as the intensity. Figure 4(b) shows ionization probability as a function of the internuclear separation, and we can see from the figure that the second electron ionization occurs at a shorter internuclear separation as the intensity increases. The calculations in both Figs. 4(a) and 4(b) show that there exists a strong intensity dependence for KER in sequential double ionization, and this is consistent with our experimental results for parallel ionization in $O(1,1)$ in this paper. Although our simplified calculations do not necessarily represent the exact experimental conditions, the consistency between our experimental results and numerical simulations suggest that the dependence of KER can be an important indicator to distinguish sequential versus nonsequential ionization in molecules.

In summary, we study NSDI in molecular fragments of N_2 and O_2 for laser polarization aligning either parallel or perpendicular along the molecular axis. In O_2, we find that NSDI can be turned on and off when we simply switch the laser polarization between perpendicular and parallel ionization. Furthermore, we find that the dependence of KER on intensity can be used to distinguish sequential versus nonsequential ionization in molecules. Both our experimental results and numerical calculations show that a stronger intensity dependence of KER corresponds to a lower NSDI rate, while a weaker intensity dependence of KER corresponds to a higher NSDI rate. The results in this paper allow us to gain a better understanding of the role of NSDI in molecular dissociative ionization.

The research was supported by the U.S. Air Force Office of Scientific Research.

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