Strong-field dissociative Rydberg excitation of oxygen molecules: Electron-nuclear correlation

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We experimentally investigate strong-field dissociative Rydberg excitation (DRE) of O2 molecules by using the photoelectron photoion coincidence spectrum, in which the outgoing neutral Rydberg fragments created by the strong laser fields are postionized by the weak static dc field of the spectrometer and afterwards detected as charged particles. The peak positions of the sum-kinetic energy release spectrum of the ejected nuclear fragments and electrons of the dissociative single ionization (DSI) channel are measured to be similar to that of the DRE channel, although their nuclear KER spectra are distinct. It indicates that the same number of photons is absorbed by the molecule in accessing the DRE and DSI channels, which are partitioned by the electron and nuclear fragments with various proportions. Different pathways towards the DRE and DSI channels are discussed based on the correlated dynamics of the nuclear fragments and electrons. Our results show that the DRE channel observed here is mostly accessed by the multiphoton resonance excitation process.

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I. INTRODUCTION

Atoms and molecules exposed to external field can be excited into Rydberg states, which have attracted much attention for their important applications in the fields of quantum information [1–4], long-range many-body interaction [5–7], precision measurements [8], neutral particle acceleration and deceleration [9,10], and high-harmonics generation [11,12]. As compared to the single-photon resonant excitation, Rydberg atoms or molecules were recently observed in strong laser fields via electron recapture [13–18] or multiphoton resonant excitation [19–22]. The photon excitation-created neutral Rydberg atoms or molecules that afterwards can be field ionized and measured as charged particles by applying a time delayed pulsed static electric field [23,24] or using the photoelectron photoion coincidence (PEPICO) spectrum [25–27]. For the dissociative frustrated double ionization (FDI) of molecules, the neutral Rydberg fragment with a certain kinetic energy and internal potential energy can be directly detected by the microchannel plates (MCPs) featured with a much longer time of flight (TOF) as compared to the photoionization-created charged ions [15,18]. To get insight into the dissociative FDI of a molecule, a complete measurement of the photoelectron, ionic, and neutral Rydberg nuclear fragments from the same molecule was performed [28,29], which unambiguously identifies the dissociative FDI channel and most importantly allows us to reveal the critical role of electron-nuclear correlation [30]. As compared to the previously observed dissociative FDI channel, the lowest order of the dissociative Rydberg fragmentation channel is associated with the dissociative single ionization (DSI) by producing a neutral and an excited Rydberg nuclear fragment, named as the dissociative Rydberg excitation (DRE) channel. This DRE channel should be most likely to be accessed for its low excitation energy, but yet lacks direct experimental observation. It is mainly because the unexcited neutral nuclear fragments cannot be detected and thus their study is experimentally more challenging than that of the dissociative frustrated double or multiple ionization channels.

In the present work, we experimentally explore the DRE of O2 molecules by postpulse static dc-field ionization of the photon excitation-created Rydberg fragments, i.e., O2 + n\hbar\omega \rightarrow O + O^+ + e^−, denoted as the O2(∗→ 1, 0) channel. As schematically illustrated in Fig. 1, the O2 molecule dissociates into a neutral atom O and an excited Rydberg fragment O∗ by absorbing multiple photons from the ultraviolet femtosecond laser fields (DRE channel). The Rydberg fragment O∗ is afterwards ionized by the weak static dc field of the spectrometer (labeled E field) and the generated charged particles of O+ and e− are detected by two MCP detectors at the opposite ends of the spectrometer. By comparing the features of the kinetic energy spectrum with that of the DSI channel, i.e., O2 + n\hbar\omega \rightarrow O + O^+ + e^−, denoted as the O2(1, 0) channel, where the electron is released in the strong laser fields, the multiphoton resonance excitation is recognized as the scenario to access the DRE channel.

II. EXPERIMENTAL SETUPS

The measurements were performed in a standard reaction microscope of cold target recoil ion momentum spectroscopy (COLTRIMS) [31–33] as schematically illustrated in Fig. 1. A linearly polarized (along the y axis) ultraviolet femtosecond laser pulse centered at 395 nm was produced by frequency doubling a near-infrared pulse from a multipass amplifier Ti:sapphire laser system (25 fs, 790 nm, 10 kHz) in a
150-μm-thick β-barium borate crystal. We focus the laser pulses onto a molecular beam by a concave reflection mirror (f = 75 mm) inside the ultrahigh-vacuum apparatus. The molecule beam propagates along the +y direction with a jet velocity of about $6.77 \times 10^{-4}$ mm/ns, leading to an offset along the y axis depending on the TOF of the measured ions in the raw data. For the convenience of the data analysis, this jet velocity was subtracted by applying a TOF-dependent linear correction of the y offset in the off-line data analysis process. The peak intensity of the laser field was measured to be $I_0 \sim 4.0 \times 10^{13}$ W/cm$^2$ with a corresponding Keldysh parameter of 3.3, and thus in the multiphoton ionization regime. The produced ions and electrons were accelerated and guided by the weak static electric field of the spectrometer (8.7 V/cm) and magnetic field (8.8 G), which were detected in coincidence by two time and position sensitive MCP detectors at the opposite ends of the spectrometer. The three-dimensional momenta of the detected ions and electrons were reconstructed in the off-line analysis based on the measured TOF and positions of the impacts.

### III. RESULTS AND DISCUSSIONS

The typical PEPICO spectrum of O$_2$ molecules in a linearly polarized ultraviolet laser field is displayed in Fig. 2(a), where the electrons released by the strong laser field or static dc field of the spectrometer can be clearly distinguished. Taking the detected O$_2^+$ cations as an example, the main peak centered at electron TOF of $57$ ns ($T_{s0}$) and ion TOF of $5826$ ns represents the photoionization in the strong laser fields, which serves as the reference for the postpulse dc-field ionization. The events of postpulse dc-field ionization of highly excited Rydberg O$_2^+$ appear along the diagonal of the PEPICO spectrum with a slope of 1 (between two red dotted lines), which is very similar to previous experiments in Ar atoms [26,27]. In the presence of the weak static dc field of the spectrometer, the excited Rydberg atoms with high principal quantum numbers have a certain probability to be ionized. The lowest principal quantum number ($n_F$) of an excited Rydberg atom that may be ionized in a static dc field can be estimated by using the saddle-point approximation of the field ionization threshold $F_{dc} = 1/16n_F^2$ in atomic units, and the diabatic field ionization formula $F_{dc} = 1/9n_F^2$ might be more appropriate as it incorporates the effect of a linear Stark shift [17,23,26]. Based on this formula, the Rydberg atoms with $n > n_F \approx 90$ are accessible to be ionized by the static dc field of the spectrometer in our experiment. As displayed in Fig. 2(a), the process of postpulse dc-field ionization of highly excited Rydberg particles is not restricted to O$_2^+$ molecules but can also be observed in the O$^+$ fragments leading to the measured events between two blue dotted lines. The horizontal line centered at ion TOF of $5826$ ns in Fig. 2(a) is a result of the false coincidence events, and is excluded in the data analysis process.

As shown in the PEPICO spectrum in Fig. 2(a), the detected ionic fragments O$^+$ coming from either the O$_2(1,0)$ or O$_2(1^+,1,0)$ channels are distinguished with the correlated electron TOF being less than $80$ ns or longer than $100$ ns, respectively. The probability to observe ionic fragments O$^+$ from dissociative double or multiple ionization channels would be orders of magnitude lower than that of the DSI channel due to the low laser field intensity in our experiments and thus negligible. Figures 2(b) and 2(c) (blue line) show the momentum distributions and kinetic energy release spectrum of the nuclear fragments (labeled as $E_N$) of the O$_2(1^+,1,0)$ channel, which are reconstructed by solving...
the corresponding Newton’s equations of $P_{\text{ion}} = M_{\text{O}} \omega_{\text{ion}} / T_{\text{ion}}$ and $P_{r} = (M_{\text{O}} + e^2 q E_{\text{ion}} - e T_{\text{elec}} + T_{\text{elec}})^2 / T_{\text{ion}}$. Here $T_{\text{elec}}$ is the TOF of the electron, $T_{\text{ion}}$ is the TOF of the ion, $L_{\text{on}}$ is the position of the ion hitting the detector, $L_{r}$ is the distance between the interaction zone of the strong laser fields and the ion detector, $E_{r}$ is the strength of the applied static dc electric field of the spectrometer, $M_{\text{O}}$ is the mass of the ionic fragment $O^+$, and $q$ represents the charge state of the ion. The tiny recoil momentum of the freed electrons from the $O^+$ fragments is negligible, and thus the momentum distributions and $E_{\text{N}}$ spectrum of the $O_2$ ($^1 \Sigma_g^+$) channel is the same as that of the DRE channel before the $O^+$ is field ionized into $O^+$ by the static dc field of the spectrometer. According to the frustrated tunneling ionization scenario [15–18,28,29], i.e., the DRE channel is produced from the DSI channel by recapturing the tunneling photoelectron at the end of a strong laser pulse, these two channels should have almost the same $E_{\text{N}}$ spectrum. However, as plotted in Fig. 2(c), the $E_{\text{N}}$ spectrum of the DSI channel (red curve) clearly differs from that of the DRE channel and thus excludes the electron recapture scenario.

On the other hand, the multiphoton resonance excitation scenario was recently demonstrated as a general mechanism to populate the Rydberg states of the nuclear fragments of breaking molecules in strong laser fields by considering the total kinetic energies of all the ejected particles [30]. In such processes, although the $E_{\text{N}}$ spectra of the ionization and corresponding Rydberg excitation channels are distinct, the peak locations of the sum-kinetic energies of all the electrons and nuclear fragments of these two channels are similar, which indicates that the same number of photons is absorbed by the molecule in accessing two different channels. The sum-kinetic energy of the ejected electrons and nuclear fragments of the DSI and DRE channels induced by the strong laser field is given by $E_{\text{sum}} = E_{\text{N}} + E_{r} = E_{\text{N}}^0 + E_{r} \approx n \hbar \omega - D_{\text{r}} - U_{\text{r}}$ for the DSI channel, and $E_{\text{sum}} = E_{\text{N}} = E_{\text{N}}^0 + E_{r} = E_{\text{N}}^0 + E_{r} \approx n \hbar \omega - D_{\text{r}} - U_{\text{r}}$ for the DRE channel. The kinetic energy of the electron in the $O_2$ ($^1 \Sigma_g^+$) channel is negligible, because it is not accelerated by the laser field. Here, $n$, $U_{\text{r}}$, $D_{\text{r}}$, and $E_{r}$ denote the number of absorbed photons with energy of $\hbar \omega$ ($\sim 1.15$ eV), the ponderomotive energy of the electron in the oscillating laser field or the ac-Stark shift of the potential energy curve of the molecule ($\sim 0.5$ eV for the ultraviolet laser field in our experiments), and the corresponding dissociation limitations of the DSI and DRE channels, respectively. The kinetic energy of the neutral fragment $O$ (not detected directly by the detector) is calculated according to the recoil momentum of the detected $O^+$ ejected from the same molecule.

According to the above discussion, the peak positions of the $E_{\text{sum}}$ spectrum of the DSI channel should be similar to that of DRE channel in the multiphoton resonance excitation scenario. As displayed in Fig. 3(a), similar $E_{\text{sum}}$ spectra, in particular the energy locations of discrete peaks, are observed for the DSI and DRE channels. The similar peak positions of the discrete $E_{\text{sum}}$ spectra indicate that the $O_2$ molecule absorbs the same number of photons in accessing two different channels, where the absorbed photon energy above the ionization threshold is mostly carried by the freed electron in the DSI channel as compared to the DRE channel for which only the nuclear fragments carry the absorbed photon energy. As a consequence, the nuclear fragments of the DRE channel are featured with a higher $E_{\text{N}}$ than that of the DSI channel, as displayed in Fig. 2(c).

In order to understand different pathways towards the DRE channel, we first analyze the dissociation pathways in the DSI channel. Figure 3(b) shows the joint energy spectrum (JES) of the coincidently measured electrons and nuclear fragments of the DSI channel. The $E_{\text{N}}$ distributions integrated over all electron energies of the DSI channel are plotted in Fig. 2(c). The multiple diagonal lines in the electron-nuclear JES indicate the photon energy sharing between the emitted electrons and nuclear fragments, which means that absorbed photon energy is not only deposited to the outgoing electron, but also transferred to the nuclear fragments via their interaction. The horizontal lines in Fig. 3(b) indicate the population of various vibrational states of the molecular cation as observed in CO molecules [34,35]. However, different from the simplest $H_2$ molecules [36,37], various molecular orbitals and electronic states may be involved in the DSI of the $O_2$ molecule, leading to a superposition of several sets of structure in the electron-nuclear JES. Figure 3(c) shows the relevant potential energy curves of the $O_2^+$. Removal of an electron from the highest occupied molecular orbital (HOMO) leads to the population of the tightly bound ground state $X^2 \Sigma_g^+$ (not shown here), mostly forming the nondissociative molecular cation $O_2^+$. However, the $a^4 \Pi_a$ state is populated by removing an electron from the HOMO-1 by absorbing six photons, which is more likely photon coupled to various dissociative states and...
generates neutral and ionic nuclear fragments with different $E_N$ values [38–40].

According to the selection rules of the dipole transition [40], the DSI of O$_2$ molecule with $E_N > 0.6$ eV may be accessed via three different pathways, as illustrated in the simplified transition scheme in Fig. 3(c). The photon-ionization-created nuclear wave packet on the $a^1\Pi_u$ state can be one, two, and three photons coupled to the $f^4\Pi_g$, $2^4\Pi_u$, and $4^4\Pi_g$ repulsive states followed by immediate dissociation to different limits and ending with $E_N$ values centered at 1.0, 2.3, and 4.2 eV, respectively. The first-order $E_{sum}$ values corresponding to the three different $E_N$ are centered at 2.8, 4.1, and 6.1 eV, respectively. It should be noted that a multiorder $E_{sum}$ spectrum spaced by the photon energy was observed in the same pathway in previous above-threshold dissociative ionization experiments [34–36]. Different from the high-$E_N$ region, however, the low-$E_N$ (<0.6 eV) region is most likely produced in the following pathway: removal of an electron from the HOMO-2 by absorbing seven photons and one of the quartet states, for instance, the $b^4\Sigma_g^-$, is populated [39], which will finally dissociate through the $b^4\Sigma_g^-$ state ending with $E_{sum}$ centered at 1.0 eV. By considering different numbers of absorbed photons and dissociation limits, the expected $E_{sum}$ of the $b^4\Sigma_g^-$, $f^4\Pi_g$, $2^4\Pi_u$, and $4^4\Pi_g$ states are 0.9, 2.7, 4.0, and 5.9 eV, respectively, which agrees with the experimentally observed values.

As mentioned above, the absorbed photon energy is deposed to the nuclear fragments in the DRE channel and thus the DSI and DRE channels should have similar peak positions of $E_N$ when $E_s$ is closed to zero for the DSI channel as shown in Fig. 3(a) (black dots), which implies the correlation between electrons and nuclear fragments. In analogy to the DSI channel, for the DRE channel, the neutral O$_2$ molecule in the ground state that absorbs seven, seven, eight, and nine photons from the strong laser fields will populate four different Rydberg states (very close to the $b^4\Sigma_g^-$, $f^4\Pi_g$, $2^4\Pi_u$, and $4^4\Pi_g$ states) followed by immediate dissociation, generating fragments O and O$^+$ with $E_N$ centered at 0.9, 2.8, 4.0, and 6.2 eV, respectively. For instance, the neutral O$_2$ molecule in the ground state may absorb seven photons to populate the excited Rydberg state (very close to the $f^4\Pi_g$ state) with a dissociation limit 18.8 eV. According to the formula $E_{sum} = E_N = E_D^O + E_D^O + n\hbar\omega - D_n - U_p$, an $E_N \sim 2.7$ eV is expected which agrees with the observed $E_N$ of 2.8 eV.

IV. CONCLUSION

In summary, we experimentally identified the DRE channel of O$_2$ molecules from the DSI channel in the PEPICO spectrum, which provides us a powerful tool to investigate the energetically lowest-order Rydberg fragmentation process of molecules in strong laser fields. Different dissociation pathways towards the DSI and DRE channels involving various bound and repulsive states of the O$_2$ molecule are discussed. The multiphoton resonance excitation is recognized as the mechanism in accessing the DRE channel. Our present work will simulate more investigations on the strong-field dissociative Rydberg excitation in molecular systems.

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