We experimentally investigate laser-induced dissociative recombination of CO$_2$ in linearly polarized strong laser fields with coincidence measurements. Our results show laser-induced dissociative processes with electron recombination after laser-induced double ionization. After double ionization, one electron can recombine to one of the two ionic fragments during laser-induced molecular dissociation. Our measurements reveal that the recombination probability of the second ionized electron is three times as high as that of the first ionized electron.

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as $\text{CO}_2 \rightarrow \text{CO}^+ + \text{O}^+ + e$ (Ch4) or $\text{CO}_2 \rightarrow \text{CO}^+ + \text{O}^+ + 2e$ (Ch5) (see Table I for channel definitions). With the reaction microscope, we achieve complete coincidence detection of the three particles (an ion, a neutral, and an electron) generated in these LIDR processes. Figure 1(b) shows the measured photoion photoion coincidence (PIPIO) distribution. The sharp parabolic PIPIO lines are signals of two-body dissociation channels as indicated in the figure, among which the LIDR channel Ch4 can be clearly identified. The weak LIDR channel Ch5 is not visible on the intensity scale of Fig. 1(b). However, after applying coincidence selection on the momentum sums of the two particles ($|p_{1z} + p_{2z}| < 4$ a.u., $|p_{1y} + p_{2y}| < 8$ a.u. and $|p_{1z} + p_{2z}| < 3$ a.u.), the two LIDR processes can be selected out from the PIPIO distribution, as shown in Fig. 1(c). The simulated PIPIO lines in Fig. 1(c) represent for the corresponding processes, which confirms the observation of the two LIDR processes. The branching ratios of related processes are summarized in Table I. In the following, we will focus on Ch4 first.

As shown in the inset of Fig. 1(b), no LIDR signals are detected with circularly polarized light. This observation contradicts a previous experimental observation of hydrogen [25], in which Rydberg states are formed via resonant multiphoton excitation by irradiation of the circularly polarized laser fields. The observation of no LIDR signals with circular pulses confirms that Rydberg states are formed through frustrated double ionization in this work, which is a rescattering-like process [9,10,23,24,26]. This process will be strongly suppressed by circularly polarized laser fields [6,27–29].

To gain insight into the quantum states involved in our observations of laser-induced dissociation of CO2, we performed quantum chemical simulations to obtain the potential energy curves of the relevant states. Multiconfiguration complete-active-space self-consistent field theory (CASSCF) should be employed for an accurate description of the electronic structure of CO2 in excited states. To simulate the dissociation processes of CO2, CO+2, and CO2+ along the C-O stretching coordinates in highly-excited states, a multistate complete active space perturbation theory of second order (MS-CASPT2) [30], which further considered dynamic correlations, was carried out using Molcas 8.2 [31]. In the active spaces of CASSCF calculations, 10, 9, and 8 electrons in 15 orbitals are included in CO2, CO+2, and CO2+ molecules respectively, when they were all kept in C2v symmetry. In searching for potential energy curves along C-O bonds of CO2+, the state-averaged CASSCF wave functions for 20 singlet excited states were used in MS-CASPT2 calculations with ANO-RCC-VTZP basis set, while O-C-O valence angles were constrained to 180°. The calculated potential energy curves (PECs) of CO2, CO+2, and CO2+ along the C-O bonds are presented in Fig. 2.

When CO2 interacts with a strong laser field, single or double ionization may occur by removing of one or two valence electrons. Since the energy gaps between different molecular orbitals (MOs) are rather small, direct removal of electrons from a low-lying MO is possible, resulting in electronically excited states [32,33]. As shown in Fig. 2, removal of one or two electrons from the HOMO of CO2 leads to stable ground states of the CO+2 or CO2+, observed as Ch1 or Ch2. On the other hand, dissociative electronically excited states of cation or dication can be reached through removal of at least one electron from low-lying MOs, yielding Ch3, Ch6, and Ch7. In the strong field interaction, high-lying Rydberg states can be populated through the so-called frustrated field ionization [9,10,23,26]. In case of molecules, such Rydberg states can be dissociative and close to the ionization threshold.

<table>
<thead>
<tr>
<th>Channels</th>
<th>Dynamics</th>
<th>Linear</th>
<th>Circular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ch1</td>
<td>$\text{CO}_2^+ + e$</td>
<td>24.52%</td>
<td>46.38%</td>
</tr>
<tr>
<td>Ch2</td>
<td>$\text{CO}_2^+ + 2e$</td>
<td>14.10%</td>
<td>1.60%</td>
</tr>
<tr>
<td>Ch3</td>
<td>$\text{CO}_2^+ + \text{O}^+ + 2e$</td>
<td>8.01%</td>
<td>5.62%</td>
</tr>
<tr>
<td>Ch4</td>
<td>$\text{CO}_2^+ + \text{O}^+ + e$</td>
<td>0.10%</td>
<td>–</td>
</tr>
<tr>
<td>Ch5</td>
<td>$\text{CO}_2^+ + \text{O}^+ + e$</td>
<td>0.002%</td>
<td>–</td>
</tr>
<tr>
<td>Ch6</td>
<td>$\text{CO}_2^+ + \text{O}^+ + e$</td>
<td>16.38%</td>
<td>12.65%</td>
</tr>
<tr>
<td>Ch7</td>
<td>$\text{CO}_2^+ + \text{O}^+ + e$</td>
<td>36.87%</td>
<td>33.75%</td>
</tr>
</tbody>
</table>
to a higher charged state, schematically shown in Fig. 2, where a high-lying Rydberg state of CO$_2^+$ lies very close to one PEC of an electronically excited state of CO$_2^+$. The kinetic energy release (KER) of the dissociation from these two states is similar because of negligible influence of the Rydberg electron to the dissociation process.

Since the measured momentum/energy distributions of detected particles contain information on the nuclear dynamics during strong field interaction, we first checked measured momentum and KER distributions of dissociation channels. The momentum distributions of the fragments generated through Ch3 and Ch4 are plotted in Figs. 3(a) and 3(b). Except for different acceptance angles, the momentum distributions of both channels are similar and peak along the laser polarisation direction. Such anisotropic distributions indicate electron removal from low-lying $\sigma$-type MOs during the strong field ionization [20,21,32]. It implies that Ch3 and Ch4 originate from electronically excited states formed by removal an electron from low-lying MOs during the strong field interaction. Due to momentum conservation, the ion momenta can be derived from measured ionic momenta. Figure 4 shows the momentum distributions of Ch1 to Ch5. For the dissociative processes the momentum sums of the two fragments are analyzed. First, we compare the momentum distributions of direct ionization processes (Ch1, Ch2, and Ch3). At the laser intensity of our measurements, single ionization happens at the leading edge of the laser pulses due to saturation, which leads to a rather narrow momentum distribution. On the other hand, in case of double ionization, we notice that the momentum distribution of the dissociative process (Ch3) is broader than that of the nondissociative process (Ch2). At the laser intensity of 5×10$^{14}$ W/cm$^2$, the dominant double ionization process happens sequentially, which means the two electrons are removed one after the other [35]. As shown in Fig. 3(a), the width of the sum momentum distribution for double ionization is broader than that for single ionization. It is due to the broader momentum width of the second electron which is removed after the first ionization step. As this lower-lying MO exhibits a
larger ionization potential than the HOMO [20], dissociative double ionization (Ch3) happens at an effectively higher laser intensity. This leads to a broader momentum distribution than that of nondissociative double ionization. Now, we compare the momentum distributions of Ch3 and Ch4. It is clear that the momentum distribution of Ch4 is much narrower than that of Ch3. For Ch4 only one electron is released, with the recombination of either the first or the second ionized electron.

In the following, we will quantify the contributions of the first and second electrons to the overall recombination yield from the measured momentum widths. Since double ionization happens mainly sequentially in our experiment, it is reasonable to assume that the first ionization step is saturated. We now can use the momentum width for single ionization (Ch1) as that of the first ionization step ($w_{1}$). Then the momentum width of the second ionization step ($w_{2}$) can be derived from the sum of measured electron momentum width ($w_{1+2}$) with the relation of $w_{1+2} = \sqrt{w_{1}^2 + w_{2}^2}$. From the measured widths of the ion momentum distribution of Ch1 (1.24 a.u.) and Ch2 (2.42 a.u.), we obtain the momentum width of the second ionization step of Ch2 to be 2.08 a.u. With the knowledge that the second ionization of Ch3 is similar to nondissociative double ionization (Ch2) [20], we used the obtained momentum width of the second ionization step of Ch2 to get the momentum width of the first ionization step by removing an electron from low-lying MOs, which yields 1.92 a.u.. Since only one of these two electrons recombines during dissociative double ionization, the measured electron momentum distribution is determined by the recombination probabilities of the two electrons [$S_{\alpha \beta} = \alpha_{e1} \exp(-4 \log 2 p_{e1}^2 / w_{e1}^2) + \alpha_{e2} \exp(-4 \log 2 p_{e2}^2 / w_{e2}^2)$]. With the obtained widths of $w_{e1} = 1.92$ a.u. and $w_{e2} = 2.08$ a.u., we performed a fitting of the electron momentum distribution with $S_{\alpha \beta}$ and got the recombination probabilities of the first and second electron: $\alpha_{e1} = 23\%$ and $\alpha_{e2} = 77\%$. The result shows that the recombination probability of the second electron is about three times as high as that of the first electron. This observation agrees with previous measurements on D$_2$ [14] and argon atoms [36]. A straightforward explanation could be that the diffusion of the second electron wave packet is much less than the first electron at the conclusion of the laser field and thus it has a higher recapture probability.

In the end, we compare two LIDR processes (Ch4 and Ch5). Both the KER spectrum [Fig. 3(c)] and the ion sum momentum distribution [Fig. 4(b)] along the laser polarization of Ch5 is similar to that of Ch4, which strongly implies that the two channels undergo similar nuclear and electron dynamics. To compare with Ch4, the only difference in Ch5 is that during the dissociation one electron recombines to the CO$^+$ fragment other than the O$^+$. One clear observation is that the yield of Ch4 is much higher than that of Ch5, with a yield ratio of about 50 between electron localized to O$^+$ and CO$^+$, as shown in Table I. A straightforward explanation of this observation can be that the electronegativity of O$^+$ is higher than that of CO$^+$ which leads to a higher electron recombination probability to O$^+$. We would like to note that the dissociative recombination process observed in our experiments is differ from those performed in storage rings with CO$^+$ in the electronic ground state [2].

In summary, we experimentally investigated the laser-induced dissociative recombination processes of CO$_2$ with coincidence detection of all involved particles. The measured KER and momentum distributions allow for understanding of both nuclear and electron dynamics during the LIDR of CO$_2$. Our measurements clearly show that LIDR of CO$_2$ originates from the recombination of one electron to one of the two ionic fragments during laser-induced dissociative double ionization. An analysis of electron momentum distributions shows that the second emitted electron has a much higher probability to recombine with the ionic fragment during the laser-induced dissociative processes. Based on the findings in this work and previous works on diatomic molecules, we believe that LIDR is a general process in strong field interaction with molecules.

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