Selective Steering of Molecular Multiple Dissociative Channels with Strong Few-Cycle Laser Pulses

Yunquan Liu,* Xianrong Liu, Yongkai Deng, Chengyin Wu, Hongbing Jiang, and Qihuang Gong†
Department of Physics and State Key Laboratory for Mesoscopic Physics, Peking University, Beijing 100871, People's Republic of China

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We report that multiple dissociative channels of carbon monoxide (CO) molecules are selectively controlled using intense phase-stabilized few-cycle laser fields (4.2 fs, 740 nm, 6×10^{14} W/cm^2). The controllable emission direction of C^{2+} from charge asymmetrical dissociation and ionization of CO dications is out of phase in a linear polarized laser field. The strong coupling between the channels is explained as the competition of recollision excitation and recollision ionization in a recollision process, leading to the opposite asymmetrical property. The experimental result provides insight into high degree controlling molecular multiple dissociative processes in the time scale of electronic motion.

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Controlling quantum phenomena has been a categorical goal of physics and chemistry since the establishment of quantum mechanics, which has been significantly developed in utilizing lasers to study the dynamics of atomic and molecular systems [1–3]. The application of advanced laser technique has led to coherent control of a wide variety of photoinduced processes, i.e., fragmentation [4], bond dissociation and rearrangement [5], and deformation of molecular geometry [6]. In particular, the waveform of a few-cycle laser field, i.e., $E(t) = a(t)\cos(\omega t + \varphi)$ [$a(t)$ is the envelope amplitude, ω the frequency, and φ the carrier-envelope phase (CEP)], can be precisely manipulated [7]. This enables the basic field-assisted electron recollision process [8] in strong field physics to be steered by the specified light field. Many interesting processes that are closely related to electron recollision, e.g., high-order harmonic generation [7], high-order above-threshold ionization [9], and nonsequential double ionization [10] in atomic systems, and electron localization in molecular systems [11,12], are directly controlled by tuning the CEP.

Multiple ionization of multielectron atomic [13] and molecular [14] systems in intense laser fields is of great interest in the strong field community. In molecular ionization and dissociation processes, the ionization rate will exhibit a pronounced enhancement at a specific internuclear distance [15]. The field-induced stretching of molecules can be avoided during the ionization using few-cycle laser fields [16]. Moreover, the ionization of an asymmetrical molecular ion (HeH^{2+}) was found in theory to be enhanced when the electric field at the peak of a few-cycle laser pulse was antiparallel to the permanent dipole of a molecule [17]. The active steering of molecular multiple dissociative ionization in the time scale of electronic motion using few-cycle laser pulses will provide a striking example for coherent control.

As a typical abundant diatomic molecule in nature, CO has been the subject of many experiments using strong laser fields [18–20]. Motivated by coherent control on molecular multiple dissociative ionization, we set our efforts on studying the behavior of CO molecules in intense phase-stabilized few-cycle laser fields. In this Letter, we show that charge asymmetrical dissociation and ionization of CO dications are controllable with the variation of CEP of few-cycle laser pulses. The emission direction of C^{2+} from those two channels is out of phase in the linear polarized few-cycle laser fields. We qualitatively explain the interesting finding that the competition between recollision excitation (RCE) and recollision ionization (RCI) in an electron recollision process leads to the opposite asymmetrical dissociation. Later in this Letter, the CEP-dependent asymmetrical ionization effect is also discussed.

The linearly phase-stabilized polarized laser pulses ($\sim$ 740 nm) at a peak intensity of 6×10^{14} W/cm^2 running with a repetition of 3 kHz were applied to dissociatively ionize CO molecules. The laser pulse duration near the interaction region was ~4.2 fs (FWHM). The phase jitter was ~140 mrad. The directional emission of ionic fragments was monitored via a newly built "reaction microscopy" (for the principle, see Ref. [21]). All experiments were performed at an ion rate below 0.1 per laser pulse. This ensured that there was one less ionized or dissociative molecule in the laser focus volume. The momentum distribution, angular distribution, and energy of the ionic fragments were calculated with the position and the time of flight on the detector. The momentum resolution is about 0.02 a.u. along the time-of-flight direction and is about 0.05 a.u. in the transverse direction. The laser polarization was perpendicular to the time-of-flight direction. The CEP of laser pulses was adjusted by insertion of fused silica into the light path with a pair of wedges and was calibrated with photoelectron spectra in the plateau [9].

Many pathways can contribute to molecular multiple dissociative ionization. Here, the dominant breakup

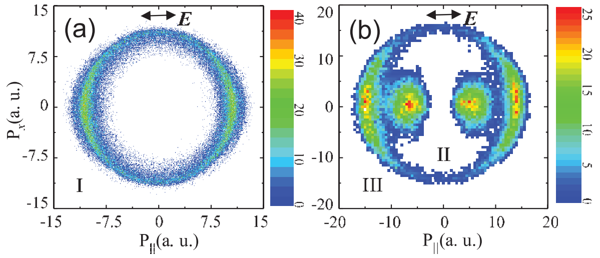

FIG. 1 (color). The two-dimensional momentum distribution of C^+ fragments from channel I (a) and of C^{2+} fragments from channel II and channel III (b) in the linear laser polarization plane.

pathways of CO^{2+} in strong laser fields are the symmetrical Coulomb explosion $CO^{2+} \rightarrow C^+ + O^+$ (channel I) and the charge asymmetrical dissociation $CO^{2+} \rightarrow C^{2+} + O$ (channel II). There are two main channels that can produce C^{2+} fragments, i.e., $CO^{2+} \rightarrow C^{2+} + O$ and $CO^{3+} \rightarrow C^{2+} + O^+$ (channel III) at the current laser intensity. Figures 1(a) and 1(b) illustrate two-dimensional momentum distribution of C^+ fragments and C^{2+} fragments from the related channels in the laser polarization plane at the phase of π. The angular distribution of C^{2+} fragment from channel II is much narrower (in the cone angle ~50° along polarization axis) as compared with the other two channels.

Although there is an abundance of work on the ionization and dissociation of CO using electron (or ion) impact and synchrotron radiation, the potential energy surfaces leading to charge asymmetrical dissociation (channel II) of CO dications have not been studied in detail thus far because it is out of scope to calculate the complicated process. The measured kinetic energy release (KER) distributions of C^{2+} fragments from channel II and channel III, as well as that of C^+ fragments from channel I, in a linear laser field (solid lines) and in a circular laser field (dashed lines) at the phase of π are illustrated in Fig. 2. There is no evident influence of the laser polarization on the KER distribution of C^+ fragments from channel I. In the experiment, the intensity of circular light is about twice as much as that for linear polarized light. The ratio of yields for those channels is suppressed about 0.52(I), 0.12(II), and 0.23(III), respectively, while using a circularly polarized light. Compared with channel I, both the yields of channel II and channel III are more suppressed.

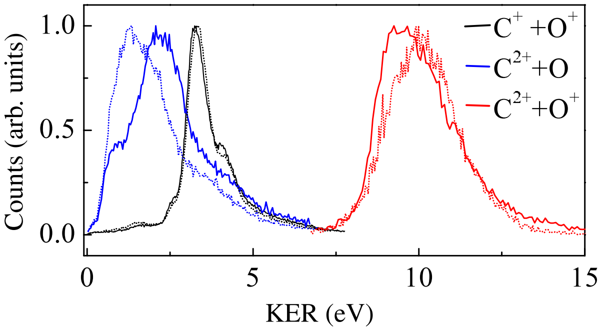

FIG. 2 (color online). The KER distribution of C^+ fragments from channel I and of C^{2+} fragments from channel II and channel III in a linear polarized (solid curves) and a circular polarized laser fields (dashed curves) at the phase of π. In order to present better comparison, the KER distribution of each ionic fragment is normalized with its own maximum counts.

The mechanism behind the laser polarization dependence is electron recollision. A more interesting question will arise, e.g., is it possible to manipulate multiple dissociative ionization of CO through the variation of CEP of laser pulses? The directional emission can be represented by the angle-integrated asymmetrical parameter $A = (P_{\rm left} - P_{\rm right})/(P_{\rm left} + P_{\rm right})$, where the measured angle-integrated ion yields in the left and right directions along the laser polarization axis are calculated with $P_{\rm left} = \int_0^{50} \sin\theta d\theta \int_0^{360} d\varphi \int dP\, P(\varphi)$ and $P_{\rm right} = \int_{130}^{180} \sin\theta d\theta \int_0^{360} d\varphi \int dP\, P(\varphi)$, respectively (we take the cone angle as 50° for all the channels). $P(\varphi)$ is the full 3D momentum distribution measured for each phase, θ is the angle with respect to the laser polarization axis, and φ is the angle in the plane perpendicular to it. In Fig. 3(a) we

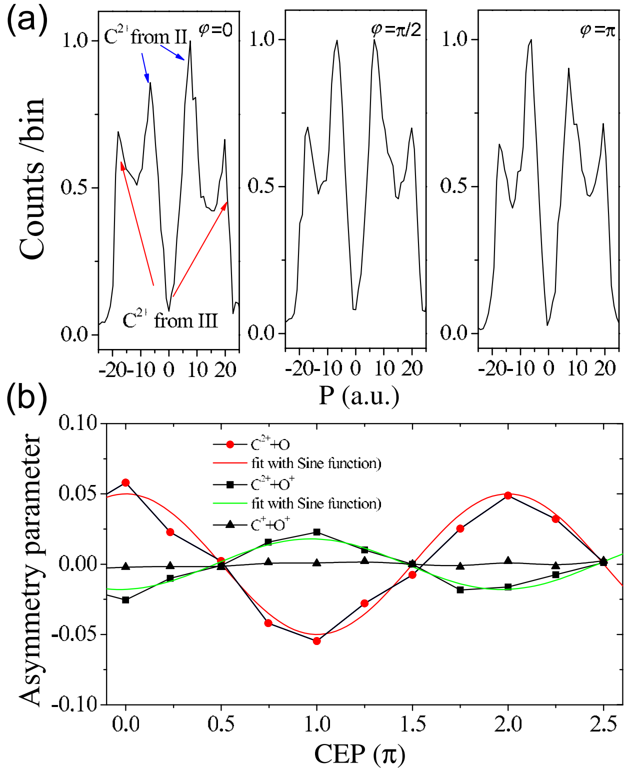

FIG. 3 (color online). (a) The momentum distribution of C^{2+} fragments from channel II and channel III in the laser polarization plane at the phases of 0, $\pi/2$, and π (in the cone of 50° in the laser polarization plane). (b) The angle-integrated (in the cone of 50° in the laser polarization plane) asymmetric parameters as a function of CEP for the three channels.

illustrate the momentum distribution of C^{2+} fragments along the laser polarization axis at the phase of 0, $\pi/2$, and π in the cone angle $\sim 50°$. One can clearly find that the emission direction of C^{2+} fragments from channel II and channel III is strongly dependent on the CEPs. Figure 3(b) shows the evolution of the asymmetry parameter A as a function of the CEP for all the channels in the same cone angle ($\sim 50°$) along the laser polarization axis. The asymmetrical parameter of C^{2+} fragments from both channel II and channel III oscillate with the CEP of laser pulses. This represents that the dissociation and ionization of CO dications can be controlled with the well-defined asymmetrical laser fields. The analysis does not include the effect of spatial averaging of CEP in relation to Gouy phase shift because it does not change the CEP dependence of asymmetry [9,11]. The peak contrast of the oscillations is about 5% for channel II and is about 3% for channel III. More interestingly, the emission direction of C^{2+} fragments from those two channels is out of phase in the linear polarized laser field.

Typically, due to the large density of states, already for the relatively small molecules, it is extremely difficult to describe the dynamics of double or triple ionization of molecules quantitatively. It still represents a great challenge to quantum chemical theory, not only because of the increased number of reaction channels, but also due to the larger possibility of multiple electronic excitations and transitions.

In order to illustrate a consistent explanation for the interesting findings, we present a qualitative picture, as shown in Fig. 4(a), where only the lowest potential energy surfaces of CO, $(CO)^+$, $(CO)^{2+}$, and $(CO)^{3+}$ are included. The potential curves are partially taken from [22]. First, at the rising edge of the laser pulse, one electron will be easily removed from the outer orbitals of the neutral molecule at the current laser intensity. When the maximum light field is around, another nonbonding electron will tunnel out. This will launch a nuclear wave packet in the bound states of CO dication. The tunneling electron can be guided back by the laser field near the zero crossing of the light field, and then it will scatter with doubly charged molecular ion. As a result, the CO dication will be excited to higher electronic states to initiate asymmetrical dissociation, or be ionized into the trication to start explosion by the returning electron wave packet. It should be noted that the excited states of the dication that are populated vertically in the Franck-Condon region are above the asymptotic limit of channel I.

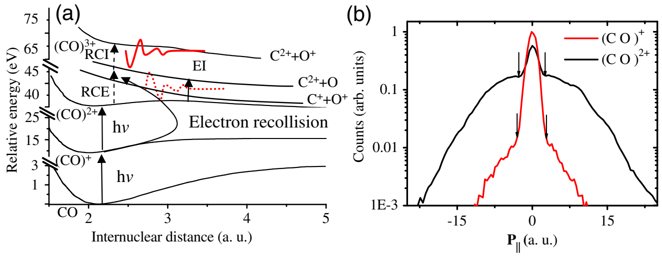

FIG. 4 (color online). (a) The schematic view of multiple dissociative pathways of CO in an intense laser field (RCE, recollision excitation; RCI, recollision ionization; EI, enhanced ionization). The dissociation and ionization of $(CO)^{2+}$ are triggered by RCE and RCI, respectively. The dotted and solid curves represent the temporal evolution of the yield probability of C^{2+} fragments for channel II and channel III in a few-cycle laser field, respectively. (b) The momentum distributions of $(CO)^+$ and $(CO)^{2+}$ in the laser polarization plane. The yields are normalized with the maximum count near zero momentum of $(CO)^+$.

The returning electron wave packet contains the information of the waveform of the laser field. The collision of the CEP-dependent electron wave packet will induce a directional movement of the parent molecular ion. If the lower bounded states of CO dication are excited by the returning electron wave packet, this will lead to a larger possibility of dissociating into channel II. Thus, it is dominated by RCE. When the returning electron takes enough energy, it can kick out another electron to produce the trication, and channel III will be dominated by RCI.

The absolute maximum asymmetry of channel II and channel III is expected at the phase of $n\pi$, i.e., the waveform of the laser field is cosine or minus cosine. But they are out of phase. This implies that C^{2+} fragments from channel II and channel III after the electron recollision move into opposite directions after collision. The strong coupling of the returning electron and molecular ion gives the contribution to the asymmetrical dissociation effect. The yield possibility of C^{2+} fragments introduced by RCE and RCI is competing because only one dissociative molecule is involved in the interaction process. This could lead to opposite asymmetrical effect of channel II and channel III. Since it needs more recollision energy to reach CO trication, the asymmetrical amplitude of channel III is slightly smaller than that of channel II. It is worth noting that channel I is also possibly reached by the RCE process. However, the asymmetry of channel I is washed out because it requires much lower energy than channel II.

In addition to RCE and RCI mechanisms, there are two other possibilities that can induce the asymmetrical dynamics of molecules, i.e., angular dependence of ionization probability and laser-induced coherent population transfer between different excited states. Before starting dissociation or ionization of $(CO)^{2+}$, the molecular ion has the same interaction environment for those two channels, i.e., the same highest occupied molecular orbital and the same orientation. Thus, if the angular dependence of ionization probability is the main role, we could expect that the cross sections of ionization and excitation of CO dication in a linear laser field have a similar angular distribution, and thus the asymmetrical property of those two channels is expected to be "in phase." Moreover, because there are much more close lying excitation states of $(CO)^{2+}$

compared with $(CO)^+$, the electron localization and the population transfer between excitation states or predissociation states will be largely reduced due to fast decay. Consequently, they are unable to explain the opposite dissociation effect.

Experimentally, three observations support such an interpretation. First, using circular polarized light at about twice the intensity as for linear polarization, this will suppress electron recollision. Experiment reveals distinct suppressed yields of C^{2+} fragments from channel II and channel III while using circular polarized laser pulses. Although the suppression effect is not so pronounced, this manifests its effect on the smaller asymmetry amplitude. Second, the KER distributions of those two channels are modified into the opposite direction with a linear polarized field assuming that a circular laser field has the similar influence on both channels. Only the competition between RCE and RCI could introduce the opposite asymmetry. Third, we illustrate the momentum distributions from $(CO)^+$ and $(CO)^{2+}$ in the laser polarization plane in Fig. 4(b). The momentum distribution of $(CO)^{2+}$ looks similar to that of $(CO)^+$. Both of them have a momentum cutoff around $2(U_p)^{1/2}$ [$\sim 2U_p$ in energy domain, $U_p = (E_0/2\omega)^2$ is the ponderomotive potential, where E_0 is field amplitude and ω is frequency] and have an evident plateau, which are the typical indications of electron rescattering in strong laser fields [23]. The plateau of momentum distribution of $(CO)^{2+}$ is enhanced about one order than that of $(CO)^+$ duo to a larger cross section of scattering. It implies that the rescattering process facilitates the dissociation or ionization of CO dications.

In conclusion, we have shown that multiple dissociative ionization channels of complex multielectron CO molecules can be selectively steered with intense few-cycle pulses. In a qualitative picture, we explain that the controllable $CO^{2+} \rightarrow C^{2+} + O$ channel results from RCE and subsequent dissociation, and the controllable $CO^{3+} \rightarrow C^{2+} + O^+$ channel results from RCI and subsequent Coulomb explosion. The competition between RCE and RCI in an electron recollision process introduces the opposite asymmetrical property. Our study shows a way out by identifying clear mechanisms directly from the experimental observation without the need of time-dependent quantum chemical calculation. In the qualitative picture, the internal molecular nature is not taken into account. Since $(CO)^+$ is a typical heteronuclear diatomic molecular ion with a permanent dipole, the CEP-dependent enhanced ionization should be considered [17]. The asymmetrical property of the dissociation and ionization of $(CO)^{2+}$ can be favored by the effect of CEP-dependent enhanced ionization using few-cycle laser pulses with a cosine waveform. For a sine light waveform, the left-right symmetrical laser field results in no asymmetry for both parallel and antiparallel cases. In the future, the origin of CEP-dependent enhanced ionization could be clarified with the orientated CO molecules [24]. The experiments suggest a route to control molecular multiple dissociative ionization and to selectively manipulate the outcome of chemical reactions using intense few-cycle laser pulses. The findings also bring both challenges and opportunities to time-dependent quantum chemical theory for complex molecular multiple dissociative ionization process.

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*yunquan.liu@pku.edu.cn
†qhgong@pku.edu.cn

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