

Attosecond Electron Correlation Dynamics in Double Ionization of Benzene Probed with Two-Electron Angular Streaking

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With a novel three-dimensional electron-electron coincidence imaging technique and two-electron angular streaking method, we show that the emission time delay between two electrons can be measured from tens of attoseconds to more than 1 fs. Surprisingly, in benzene, the double ionization rate decays as the time delay between the first and second electron emission increases during the first 500 as. This is further supported by the decay of the Coulomb repulsion in the direction perpendicular to the laser polarization. This result reveals that laser-induced electron correlation plays a major role in strong field double ionization of benzene driven by a nearly circularly polarized field.

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Electron-electron correlation is a ubiquitous phenomenon in many important processes, but unfortunately it is not an easily accessible one experimentally or theoretically. Attosecond spectroscopy based on single-photon absorption can provide valuable insight [1,2], albeit indirect, by following nonequilibrium electron dynamics in a time domain. Attosecond extreme ultraviolet (XUV)-pump-attosecond XUV-probe experiments face a significant technical barrier and are yet to be implemented, even though theoretical work has suggested that such experiments can directly access electron correlation dynamics by monitoring the momentum distribution of two emitted electrons [3]. On the other hand, strong field approaches such as in high harmonic spectroscopy [4,5] and strong field nonsequential double ionization [6] can induce strong correlation effects through recollision [7,8], in which an electron is first ionized by a strong laser field and is later returned to the ion core by the opposite polarity of the laser field. This reencounter between the electron and the ion results in many interesting and fundamentally important phenomena such as high harmonic generation, which is the only established method of attosecond pulse production [9]. Recollision physics has thus become the foundation of attosecond spectroscopy. To understand and manipulate the recollision process and relevant electron correlation is the key to many aspects of attosecond spectroscopy.

It has been shown that an intense circularly polarized field can suppress recollision and thus nonsequential double ionization and high harmonic generation [10,11]. As a result, sequential double ionization driven by a circular field could potentially provide information on inherent electron correlation [12] and has been studied [13–15] in the femtosecond regime with the angular streaking method [16,17], in which the ionization time is mapped onto the electrons' ejection angle. However, recent theoretical works have shown that recollision is possible even with circularly

polarized light [18,19] when the initial transverse velocity cancels out the laser-induced motion and thus brings the electron back to the ionic core. So far, only a few indirect experiments provided some evidence of this mechanism by measuring the laser-intensity-dependent double ionization rate in circularly polarized fields. A “knee” structure was interpreted as the evidence of recollision [20,21].

A pump-probe approach in the attosecond time regime will provide direct experimental evidence by measuring the time-delay-dependent double ionization rate, because recollision could lead to simultaneous ionization through impact ionization [22]. However, such a technique was not previously available, neither in a strong field nor in a weak field regime. The shortest relative time delay accessed by angular streaking was more than 1 fs [13]. This limit is imposed by a long dead time of conventional electron-electron detection techniques such as delay line anodes [23]: When two electrons arrive in proximity of each other both temporally and spatially, the second electron will be lost and thus leads to a very low detection efficiency of electron pairs with similar momentum. In the angular streaking method, this translates to the loss of information about two electrons, which are ejected within 1 fs of each other.

This limit has now been removed with the development of a new type of 3D imaging system, which features a camera and a waveform digitizer [24,25]. The physical dead time is well under 1 ns, and a zero dead-time detection has also been achieved [26]. When this new imaging system is combined with the principle of angular streaking, a relative time delay of ionization ranging from tens of attoseconds to more than 1 fs can be accessed, thus enabling a true attosecond pump-probe method, in which the pump step is the first ionization while the probe is the second ionization. Furthermore, because the new imaging system can readily obtain 3D momentum information, the momentum correlation perpendicular to the plane of

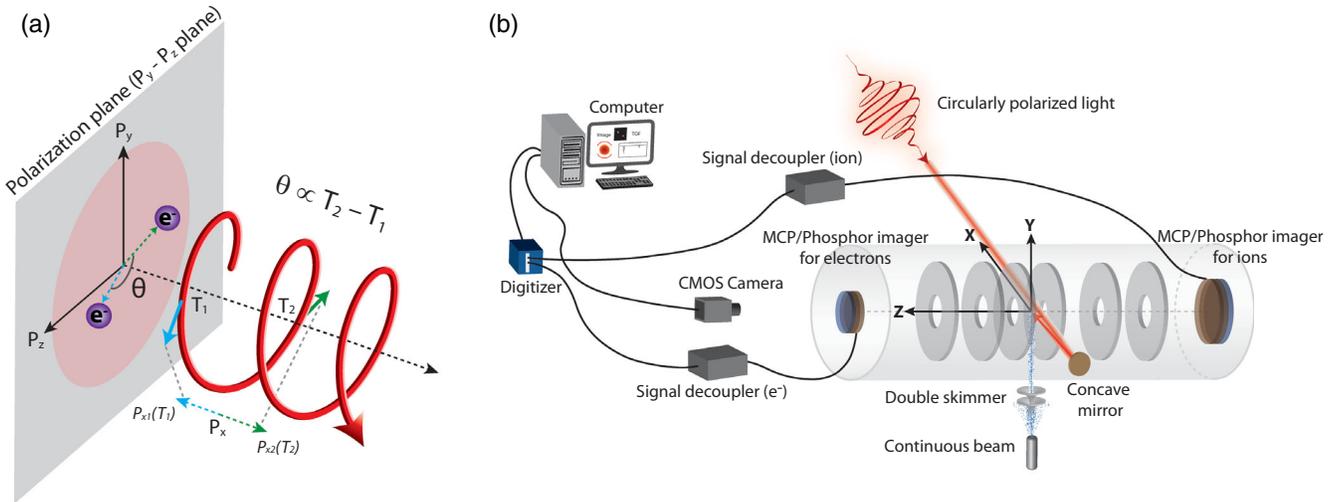


FIG. 1. (a) The basic principle of the 3D-2eAS. The ionization time delay of two electrons is mapped onto the relative ejection angle in the plane of polarization (YZ plane), while the momentum correlation in the X direction provides field-free electron correlation, which is often dominated by Coulomb repulsion at short time delays. (b) The experimental setup for 3D electron-electron-ion coincidence detection capable of attosecond pump-probe measurement. It features a 3D imaging system with a zero dead-time detection of electron-electron coincidence.

circularly polarized light is accessible, providing another dimension of information to help elucidate the electron dynamics. The principle of this 3D two-electron angular streaking (3D-2eAS) technique is shown in Fig. 1(a).

We have applied this new technique to study the time-resolved double ionization rate of a relatively large molecule, benzene (C_6H_6), in a close-to-circular laser field. The experiment was carried out in a velocity mapping coincidence apparatus [Fig. 1(b)] [27]. Briefly, this apparatus features a six-electrode ion-electron optics that can velocity focus both ions and electrons to improve momentum resolution. A 30 fs laser (800 nm) was focused onto the molecular beam by a spherical mirror mounted in the vacuum. The estimated laser intensity was $\sim 2 \times 10^{14}$ W/cm 2 . The ellipticity was estimated to be ~ 0.9 . Benzene was bubbled into the chamber by helium carrier gas through a 20-micron diameter aperture, and the beam was double skimmed before entering the main chamber. The produced ions and electrons were then directed in opposite directions by an electric field and impacted on two MCP/phosphor screen imagers at the end of their TOF regions. Only the TOF was measured on the ion side, while the new zero dead-time 3D imaging system was used to measure the 3D momentum of two coincidence electrons. The overall electron count rate was ~ 0.07 , and the false coincidence rate was estimated to be less than 20%.

The main result is shown in Fig. 2(a), in which the double ionization yield is plotted against the relative ejection angles between the two electrons in the plane of polarization. Only the electrons in coincidence with non-dissociative benzene dications are studied. Three features are seen at $\sim 25^\circ$, $\sim 85^\circ$, and $\sim 170^\circ$. Because a multicycle laser pulse (30 fs, 800 nm) was used, it is not straightforward to convert the ejection angle ($0^\circ - 180^\circ$) into an ionization time delay (0–1.33 fs). An ambiguity of

multiples of the half laser period (1.33 fs) needs to be considered. Here we turn to the momentum correlation in the third dimension (perpendicular to the plane of the polarization, i.e., X axis). Figure 2(b) shows the ratios between back-to-back events and side-by-side events along this direction against the relative angles between the electrons in the plane of the polarization. We see a higher than one ratio for small relative angles, while it decays to 1 toward larger angles. It is well established that, when electrons are ejected in close proximity (spatially and temporally) of each other, Coulomb repulsion in the final states will force electron ejection in the opposite directions, and thus back-to-back events are favored over side-by-side events [28,29]. As the time separation (distance) increases, the Coulomb repulsion becomes weaker, and the electron relative ejection direction loses preference. As shown in Fig. 2(b), the correlation between the small relative angles in the plane and the high back-to-back ejection probability in the perpendicular direction can be understood only in terms of angle-to-time correlation, as in angular streaking. This correlation suggests that the first feature (peaked around 25°) in Fig. 2(a) correlates to the double ionization events that take place within the first 500 as (~ 70). This is the first time that such a correlation is observed, and it validates the application of 3D-2eAS in probing attosecond dynamics. For the second (85°) and third feature (170°), because of the close to one ratio between back-to-back and side-by-side events, they are most likely related to the double ionization at a longer time delay possibly over a few laser cycles.

Now that we have established that the observed decay of the first feature is indeed time dependent within the first 500 as, we can examine the origin of such dynamics. Our

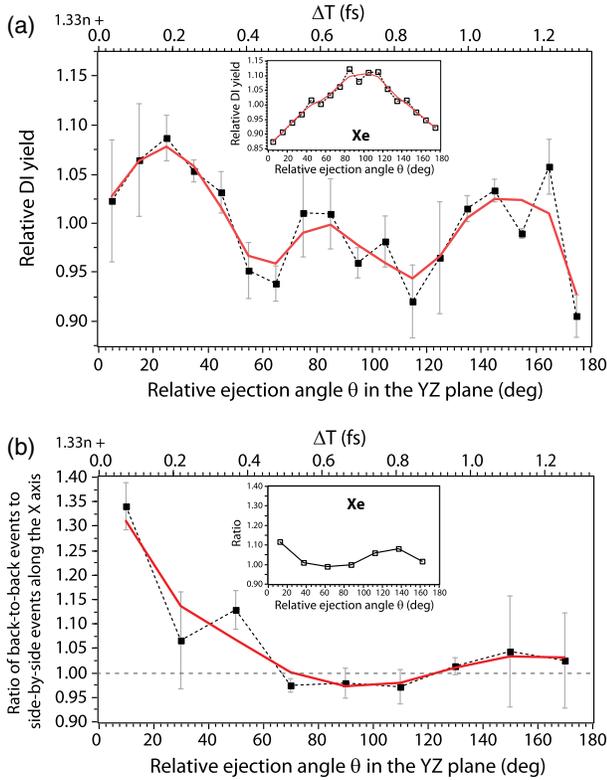


FIG. 2. (a) Angle- and time-dependent double ionization (DI) yield of benzene in intense elliptically polarized light field. The angle is defined as the relative ejection angle between electrons in the plane of polarization. The data are plotted as a relative yield between true coincidence events and false coincidence events. False coincidence events are generated by mismatching coincidence electron pairs. As a comparison, the inset shows the result of xenon double ionization, which is dominated by sequential double ionization. (b) The ratio between back-to-back and side-by-side ejection events in the direction perpendicular to the plane of the polarization. The n in the top axis label is a non-negative integer. The black curves are lines connecting data points, while the red ones are smoothed data. The inset is from xenon double ionization.

calculation assuming a sequential process and no electron correlation between the first and second electrons has failed to reproduce the trend of the time-resolved transient (see later discussion), and this suggests that a different mechanism is at play in the ionization dynamics at the short time scale (<500 as). Classical ensemble calculations have been used to highlight the role of electron correlation in strong field double ionization, and it has worked quite well for many systems [30]. Here, such a calculation is implemented to elucidate the dynamics. In this model, electron-nuclear and electron-electron interactions are represented by a 3D soft-Coulomb potential $V(r_1, r_2) = -(2/\sqrt{r_1 + a^2}) - (2/\sqrt{r_1 + a^2}) + (1/\sqrt{(r_1 - r_2)^2 + b^2})$ (in atomic units). $E_{\text{tot}} = (p_1^2 + p_2^2)/2 + V(r_1, r_2)$ is the ground state energy of benzene: -24.65 eV (the sum of the first and second ionization potentials of benzene). a and b were set to be 2.7 and 0.5, respectively. The electrons were propagated with

Newtonian equations of motion without a laser field and sampled every 0.5 a.u. (12 as) to obtain an ensemble of 10^6 initial states. For each state in the initial ensemble, the trajectories for the electrons were calculated in a circularly polarized laser electric field with a total duration of 30 optical cycles (800 nm), a sine-squared envelope, and a maximum intensity of 3×10^{14} W/cm². As soon as both electrons reached a distance of at least 6 a.u. from the ion, the time was recorded as the ionization time of the second electron t_2 . The trajectory for the other electron was then backtracked until it was just less than 6 a.u., and the time was recorded as the ionization time of the first electron, t_1 ($t_1 < t_2$). Figure 3(a) shows that the majority of the ionization events take place with delays of less than 500 as. This is a clear sign of the recollision mechanism and is further verified by a close inspection of trajectories leading to double ionization (Fig. 3 insets). Figure 3(a) also shows the angle-dependent double ionization rate, which confirms the first feature observed in the experimental transient. Finally, Fig. 3(b) shows the ratios between back-to-back

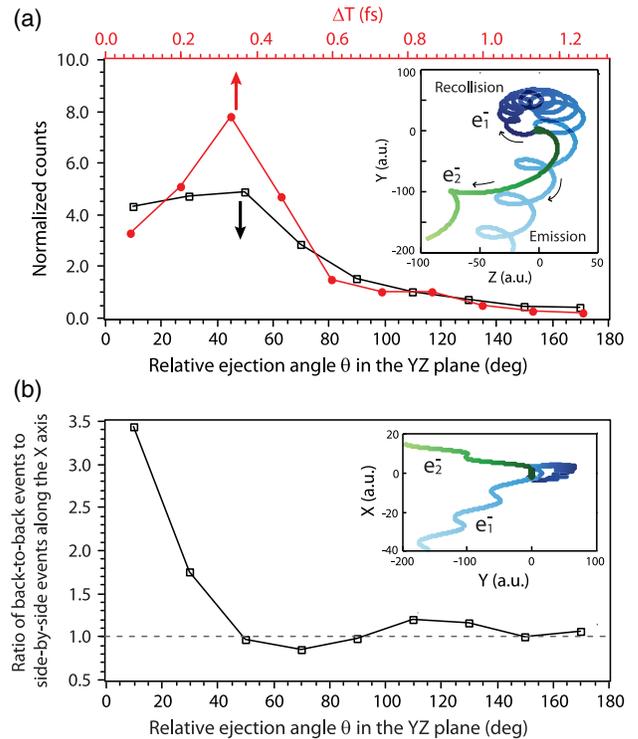


FIG. 3. (a) Angle- and time-dependent double ionization rate from classical ensemble calculations, showing double ionization preferring short time delays and small relative angles. The counts are normalized to that at 110° . The inset is a representative trajectory in the plane of polarization, showing that, after the ionization of the first electron (blue), it returns to the core and knocks out the second electron (green). (b) The ratio between back-to-back and side-by-side events in the direction perpendicular to the plane of polarization, showing at short time delays, back-to-back ejections are preferred due to Coulomb repulsion. The inset shows the same trajectory as in (a) but in the XY plane.

and side-by-side events along the direction perpendicular to the plane of polarization, which also agrees with experimental observations [Fig. 2(b)]. We note that the absolute modulation is higher in the simulation than experimentally measured values. This is because the classical calculations underestimate the contribution of sequential double ionization. Nonetheless, the general agreement between the experiment and theory shows that recollision plays an important role in double ionization driven by circularly polarized light in large molecules such as benzene.

The second feature in Fig. 2(a) is due to the orthogonal configuration of the two degenerate HOMO orbitals of the benzene: The first electron is ionized when the electric field is aligned with one HOMO orbital, and the second electron is ionized when the electric field rotates 90° and aligns with the second HOMO orbital. Because the ionization rate is high when the electric field is aligned with the orbital orientation, a peak will occur at 90°. Our molecular samples were not spatially aligned, but our calculation shows that this effect can survive the orientation averaging. A similar result was obtained with xenon double ionization (Fig. 2 insets), in which sequential double ionization dominates and the electrons are preferably ionized out of two orthogonal p orbitals [31]. Time-dependent configuration interaction with a complex absorbing potential (TDCI-CAP) [32,33] was used to model this sequential double ionization process in benzene using a seven-cycle 800 nm sine-squared pulse. Briefly, the time-dependent wave function was expanded in terms of the field-free Hartree-Fock ground state and all singly excited states of the field-free, time-independent Hamiltonian. The calculations employed the Dunning aug-cc-pVTZ basis and an absorbing basis consisting of nine sets of diffuse Gaussian functions on each atom. The time-dependent configuration interaction coefficients were propagated using a Trotter factorization of the exponential of the Hamiltonian using a time step of 1.2 as (0.05 a.u.). A set of TDCI-CAP simulations for the single ionization of benzene yielded the angle dependence of the populations of the cations resulting from removal of an electron from each of the degenerate highest occupied molecular orbitals. A second set of TDCI-CAP calculations yielded the angular dependence of ionization for each of the cations. These data were then combined to calculate the dependence of sequential double ionization on the angle between the laser polarizations for the first and second ionizations. The result is shown in Fig. 4(a) [Fig. 4(b) shows angular-dependent ionization of different orbitals of neutral and cation]. A peak is seen at 90° at two different laser intensities, in agreement with the second feature in Fig. 2(a). The observation of this feature suggests that, in addition to the extremely ultrafast time resolution, 3D-2eAS also provide spatial sensitivity on orbital orientation.

We now turn to discuss the third feature at ~170° in Fig. 2(a). As mentioned earlier, this feature is likely due to a sequential ionization mechanism because of the close to one

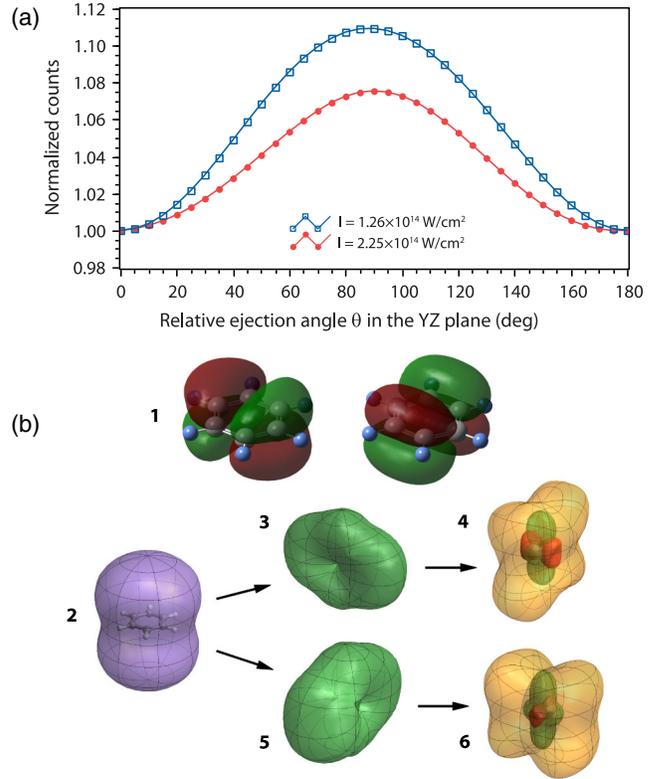


FIG. 4. (a) Calculated angle-dependent ionization rate assuming a sequential double ionization at two different laser intensities. These results explain the second feature in Fig. 2(a) at ~85° but not the first and the third feature. (b) 1. The degenerate highest occupied molecular orbitals of benzene, HOMO and HOMO-1. 2. Angular dependence of the total yield for the first ionization of benzene. 3. Angular dependence of the yield of benzene monocation resulting from the ionization of an electron in the HOMO. 4. Angular dependence of the second ionization; benzene monocation with one electron in α HOMO, α HOMO-1, and β HOMO-1 is ionized to the dication by ejection of an electron from α HOMO-1 (yellow), α HOMO (green), and β HOMO-1 (red). 5. The same as 3 but for ionization of an electron from HOMO-1 to produce benzene monocation with one electron in α HOMO, α HOMO-1, and β HOMO. 6. The same as 4 but for ionization of monocation by ejection of an electron from α HOMO (yellow), α HOMO-1 (green), and β HOMO (red).

ratio between its back-to-back and side-by-side component events in the perpendicular direction. However, the anti-correlation ejection character in the plane of polarization is very peculiar, as it would suggest a certain correlation effect between the two electrons even though their ionization times are delayed at least one half of a laser cycle. Previous nonsequential double ionization experiments on noble gases with linear polarized light have seen back-to-back ejection at low laser intensity, and this was interpreted as the result of doubly excited states produced through recollision [34,35]. However, even though we have shown that recollision is present in benzene with circularly polarized light (and thus producing doubly excited states), a similar mechanism encounters difficulty in explaining the third feature. This

is because, for circular polarized light, both its electric field and vector potential change gradually in the plane of polarization, and this would lead to uniform ionization probabilities. Here, we propose that the momentum anti-correlation arises from *strongly* correlated doubly excited states in which the excited electrons reside on the opposite side of the molecule. Possible candidates for such states are Rydberg states converging to dication states with spatially separated positive charges. The presence of similar states was previously suggested in the study of NSDI of benzene by linearly polarized light [27]. The shift of the peak position away from 180° can be attributed to the attractive interaction between ionized electrons and an ionic core and/or excitations of the second electron before ionization [17].

In summary, attosecond 3D-2eAS has achieved the long-term goal of pump-probing attosecond dynamics in the first 500 as. The technique offers a unique capability for investigating both symmetry- and time-dependent electron correlation dynamics. By choosing few-cycle pulses, it is possible to avoid recollision and carry out measurements in the sequential regime to measure inherent electron correlation dynamics. What is particularly exciting is that, by using mid-IR pulses as the driving laser, coupled nuclear and electronic dynamics can be studied continuously from zero attosecond up to tens of femtoseconds. This will bring a unification of attosecond and femtosecond spectroscopy that has been intensely pursued in the past two decades.

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