Laser-subcycle control of electronic excitation across system boundaries

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Abstract
We report on the results of a joint experimental and numerical study on the sub-cycle laser field-driven electron dynamics that underlie the population of highly excited electronic states in multiply ionized argon dimers by electron recapture processes. Our experiments using few-cycle laser pulses with a known carrier-envelope phase (CEP) in combination with reaction microscopy reveal a distinct CEP-dependence of the electron emission and recapture process and, furthermore, a small but significant CEP-offset to the scenario in which no excited argon dimers are produced. With the help of classical ensemble trajectory simulations we trace down these different CEP-dependencies to subtle differences in the laser-driven sub-cycle electron trajectory dynamics that involve in both cases the transfer of an electron from one argon ion across the system boundary to the neighboring ion and its transient capture on this ion.

Keywords: frustrated field ionization, CEP-control of electron dynamics, strong-field ionization of atomic dimers

(Some figures may appear in colour only in the online journal)

1. Introduction
One of the most intensely studied process of the last 15 years in strong-field laser–matter interaction was the control of intramolecular electron-localization during the ionization-dissociation of isolated, small molecules with tailored laser fields. Such localization was demonstrated along one spatial dimension using the carrier-envelope phase (CEP) of linearly polarized intense few-cycle laser pulses [1–5], the relative phase between different frequencies in intense multicolor waveforms [6–11], and even in two spatial dimensions using the CEP of elliptically polarized few-cycle pulses [12] or different two-dimensional intense multicolor waveforms [13–15]. More important for applications than the localization of charge within a single molecule is, however, the relocalization of charge between different molecules: charge transfer between closely-spaced molecules is the main driving action
behind immensely important processes such as photosynthesis [16, 17], photocatalysis [18–20], or solar-driven energy production [21, 22].

Recently, using the argon dimer $\text{Ar}_2$ as a model system for two closely-spaced but separate quantum entities, we demonstrated for the first time CEP-control over electron transfer reactions across system boundaries [23]. We showed that an electron emitted from one argon atom and driven to the other atom by the strong laser field, can become transiently captured before it leaves toward the detector. We called this process LITE (laser-induced transfer of an electron). In order that the transferred electron can initiate a reaction at the distant site, such as it is the case upon charge-transfer in the processes mentioned above, it is crucial that the transferred electron is not only transiently captured but becomes trapped at the acceptor site in an excited electronic state. It has been shown that population of excited states or even highly excited (Rydberg) states can entail a variety of molecular reactions. In the simplest case this can lead to the breakage of a bond in the excited molecule [24–28]. However, it can also initiate extremely complex dynamics. For example, the transfer of an electron can entail bond-breaking in the donor or acceptor molecule coupled with the transfer of a (radical) moiety to or from the acceptor molecule [29–32], a process of fundamental importance across many areas of chemistry and biology.

It has been shown in many experiments that also this process, the population of Rydberg states, can take place in a strong laser field. In this process, known as frustrated field ionization (FFI), laser field-emitted electrons that have negligible kinetic energy after the completion of the intense laser pulse, become trapped by the attractive Coulomb potential of an atomic or molecular ion [33–46]. In detail, the trapping process not only depends on the energy of the electrons but also on the shape and orientation of their orbits. Capitalizing on this we could demonstrate control over the population of Rydberg states by FFI using orthogonal two-color (OTC) fields [44].

In this article we report on results of a joint experimental and numerical work conducted with the aim of obtaining insight into the sub-cycle laser field-driven electron dynamics that underlie the population of excited states by the FFI process in a quantum system with two separate entities. As in our previous work [23] we chose the argon dimer as our model system with two independent atoms separated by the relatively large distance of a van der Waals (vdW) bond for this investigation. In our experiments using few-cycle laser pulses with a known CEP in combination with reaction microscopy [47, 48] to record the products of the laser-dimer interaction we find a distinct CEP-dependence of the electron emission and subsequent electron trapping (or recapture) process that is responsible for the population of excited (Rydberg) states. Moreover, we find a slightly different CEP-dependence of the electron emission process in the argon dimers where no excited states are populated, which manifests itself as a small CEP-shift to the recapture case. With the help of our simulations using a three-dimensional (3D) classical ensemble trajectory model we trace down the CEP-dependencies and the CEP-shift to subtle differences in the intricate laser-driven sub-cycle electron trajectory dynamics that involve in both cases the transfer of an electron from one argon ion across the system boundary to the neighboring ion and its transient capture on this ion. Furthermore, we discuss the localization of the Rydberg electron during fragmentation of the argon dimer via Coulomb explosion.

2. Experiments

In our experiments, the supersonic expansion of a few bars of argon gas into an ultra-high vacuum chamber produces a dilute gas jet that contains a small fraction (few percent) of vdW-bound argon dimers. The gas jet, propagating along the $x$-direction of the lab coordinate system, is intersected in the interaction chamber (background pressure $< 10^{-10}$ mbar) of a reaction microscope, also applied, e.g., in references [12, 23, 43–45], with a laser beam propagating along $y$-direction delivered by a titanium-sapphire multi-pass laser amplifier system, focused onto the gas jet by a spherical mirror with a focal length of 60 mm. The pulses in the beam were linearly polarized along $z$-direction and had an FWHM duration in intensity of 4.5 fs, a center wavelength $\lambda = 750$ nm and a peak intensity, calibrated in $\textit{in situ}$ [49], of $5 \times 10^{14}$ W cm$^{-2}$. The few-cycle laser pulses were generated by spectral broadening in a gas-filled hollow-core capillary and subsequent temporal recompression of the 25 fs pulses emerging from the laser amplifier system.

The interaction of the intense few-cycle laser pulses with the atoms and dimers in the gas jet led to ionization of the argon atoms and ionization-fragmentation of the argon dimers. The generated ions were guided over a distance of 5.7 cm toward a position sensitive multi-hit-capable detector by a weak electric field of 3 V cm$^{-1}$, where the position and time of flight (TOF) of each ion was recorded. The emitted electrons were not detected in the present experiments. From the ions’ impact positions and TOF values the 3D momentum of each detected ion was calculated. In the argon dimers, the vdW-bound argon atoms are separated by their equilibrium internuclear distance ($R_{eq}$) and upon multiple laser ionization undergo fragmentation via Coulomb explosion described by the reactions $\text{Ar}_2 \xrightarrow{\text{Laser}} \text{Ar}_2^{(n+m)+} + (n+m)e \rightarrow \text{Ar}^{(n+m)+} + (n+m)e$. We denote these different ionization-fragmentation channels that result in the production of two argon ions, $\text{Ar}^{(n,m)+}$ and $\text{Ar}^{(n,m)+}$, by $\text{Ar}(n,m)$.

In order to select a specific two-body channel $\text{Ar}(n,m)$, the density of the gas jet was kept low, such that on average less than 0.3 ions per laser shot hit the detector. Under these coincidence conditions, a specific channel $\text{Ar}(n,m)$ can be selected in the offline data analysis from the more abundant atomic ionization events by imposing momentum conservation conditions. From the many different ionization-fragmentation channels that were detected in the experiments, we were specifically interested in the channels $\text{Ar}(1,2)$ and $\text{Ar}(2,2)$.

In the experiments, the CEP of the few-cycle laser pulses was allowed to fluctuate freely and a single-shot stereo electron spectrometer in phase-tagging mode [50, 51] was used to measure the CEP of each and every laser pulse and
additionally to monitor the duration of the laser pulses [52] during the experiments. In the offline data analysis the CEP of each laser pulse was linked to the momenta of the ions detected for this pulse. The unknown constant offset value of the measured CEP values that is inherent to the phase-tagging technique was calibrated to the absolute CEP values of the simulations by overlapping the measured and simulated asymmetry values (defined below) of electron/ion emission over CEP in the single ionization channel $\text{Ar} \rightarrow \text{Ar}^+ + e^-$ of the argon monomer. Because the $\text{Ar}^+$ monomer ions are the most abundant species produced both in the simulations and experiments, the statistical error bars in the data are very small. As a result, they can be fitted by sinusoidal functions with very high accuracy. The uncertainty in the CEP obtained from these fits was about 0.005 rad and 0.003 rad for the measured and simulated data, respectively. Thus, by this procedure the unknown, constant CEP-offset of the experiment is precisely connected to the CEP-value of the simulations. Further information on the few-cycle laser setup and reaction microscope can be found in references [12, 23, 53–55].

The KER during the Coulomb explosion leading to the channels $\text{Ar}(1,2)$ and $\text{Ar}(2,2)$ was calculated from the measured momentum vectors. The KER-distributions, depicted in figure 1(a), show characteristic peaks. In each fragmentation channel, the most dominant peak can be attributed to the Coulomb explosion from the equilibrium internuclear distance $R_{eq}$ of about 7.1 a.u. and weaker peaks at higher KER [36–38]. The FFI process starts with the $n + m + 1$ times ionization of the argon atoms in the dimer. Subsequently, one of the released electrons is recaptured by the Coulomb potential of one of the two argon ions into a Rydberg state, leading to the formation of a highly excited argon ion.

In the following we will focus on the case where each argon atom is ionized two times and one of the four emitted electrons is recaptured by one of the two argon ions leading to a dimer $\text{Ar}^+ + \rightarrow \text{Ar}^{2+}$ that is composed of a dication and a highly excited singly charged ion. Upon Coulomb explosion of this dimer, the excited $\text{Ar}^+$ ion is detected as a singly charged ion in coincidence with a doubly charged ion. Thus, these Coulomb explosion events are selected as belonging to the $\text{Ar}(1,2)$ channel. However, because the Rydberg electron on the $\text{Ar}^{2+}$ with its widely extended wavefunction only weakly shields the nuclear charge, its effective charge state sensed by the neighboring ion in the dimer is not +1 but almost +2. Therefore, the mean KER value obtained during the Coulomb explosion of the $\text{Ar}^{2+} \rightarrow \text{Ar}^{2+}$ dimer is almost as high as that in the $\text{Ar}(2,2)$ channel, cf figure 1(a). We will from now on refer to this ionization-fragmentation channel as $\text{Ar}^{1,2}$. A corresponding FFI process takes place for argon dimers in the jet, from which initially three respectively two electrons are emitted from each argon atom and an $\text{Ar}^{3+} \rightarrow \text{Ar}^{2+}$ dimer is formed upon ionization. At the conclusion of the laser pulse one of the released electrons is recaptured by the $\text{Ar}^{3+}$ ion and a highly excited $\text{Ar}^{2+}$ ion is formed. The Coulomb explosion of this $\text{Ar}^{2+} \rightarrow \text{Ar}^{2+}$ dimer is reflected by the KER-peak around 23 eV in the distribution corresponding to the $\text{Ar}(2,2)$ channel.

As described above, in this work we are interested in the laser field-driven electron dynamics that underlies the electron recapture process to a Rydberg state in an argon dimer. We have shown recently in reference [23] that detailed insight into the field-driven electron emission dynamics can be gained from the CEP-dependence of the mean electron sum momentum of all emitted electrons. By this approach we could show the importance of the electron transfer process (LITE) in the ionization-fragmentation dynamics of the dimers. Motivated by this result, we adopt this approach in the present work. Because here we are interested in the combined action of the LITE and FFI-excitation processes, we compare in the following the CEP-dependencies of the mean electron momentum in the $\text{Ar}^{1,2}$ and $\text{Ar}(2,2)$ channels. Since the formation of both channels starts with the emission of two electrons from each argon atom in the dimers, but the field-driven dynamics
differs by the recapture process to the Rydberg state, it is reasonable to expect that information on the recapture process can be gained from the differences in the CEP-dependence of the mean electron momentum.

To obtain the mean electron momentum we make use of momentum conservation. Due to momentum conservation, the center of mass recoil momentum of the detected argon ions

\[ p_{Z_{n}}^{(m)} = p_{e_{k}}^{(m)} + p_{e_{n}}^{(m)} \]

is connected to the sum momentum of the emitted electrons

\[ p_{Z_{e}}^{(m)} = \sum_{i=1}^{2} p_{e_{i}}^{(m)} \]

with \( p_{e_{i}} \) the momentum of the \( i \)th electron, via the relation

\[ p_{Z_{e}}^{(m)} = -p_{R}^{(m)} \]

(for which the small photon momenta are neglected). From the measured ion momenta we can thus obtain the mean value of the electron sum momentum distribution, which for the channel \( \text{Ar}(n, m) \) we denote by

\[ (p_{Z_{e}}^{(m)}) = - (p_{R}^{(m)}) \].

As the laser field is linearly polarized along \( z \), the electrons are mainly driven along this direction and the CEP-dependence of the laser-dimer interaction can be well studied by analyzing the mean value of the center of mass ion momentum distribution along \( z \) [23], which is

\[ (p_{Z_{e}}^{(m)}) \].

However, we have shown previously, in the supplemental material of reference [23], that alternatively to \( (p_{Z_{e}}^{(m)}) = - (p_{R}^{(m)}) \) an asymmetry-parameter with the same information content can be used to quantify the electron emission. This asymmetry-parameter has the advantage that it can be directly compared to the simulated electron ionization time distributions that we will introduce in figure 3. The asymmetry-parameter is defined as

\[ A_{v,1,2}^{(m)} = \frac{n_{up}^{(m)} - n_{dn}^{(m)}}{n_{up}^{(m)} + n_{dn}^{(m)}} \]

where \( n_{up}^{(m)}, n_{dn}^{(m)} \) are the number of events with a positive (negative) electron sum momentum in \( z \)-direction in the \( \text{Ar}(n, m) \) channel. However, as in our experiments we only detected the ions, we used instead the number of events \( n_{up}^{(m)} \) with positive (negative) ion sum momentum, \( p_{Z_{e}}^{(m)} \), to calculate the asymmetry-parameter for the ions

\[ A_{v,1,2}^{(m)} = \frac{n_{up}^{(m)} - n_{dn}^{(m)}}{n_{up}^{(m)} + n_{dn}^{(m)}} \].

This asymmetry parameter is unambiguously connected to the electron asymmetry parameter analyzed in the following by

\[ A_{v,1,2}^{(m)} = - A_{v,1,2}^{(m)}. \]

The measured and simulated \( A_{v,1,2}^{(m)} \) curves over CEP for the two channels of interest, \( \text{Ar}(2,2) \) and \( \text{Ar}(1,2) \), are shown in figures 1(b) and 1(c), respectively. As a reference, the \( A_{v} \)-curves for the channel \( \text{Ar}(1,2) \) are also shown in the figures. The relatively large CEP-shift of \( A_{v} \) between the channels \( \text{Ar}(1,2) \) (black curve) and \( \text{Ar}(2,2) \) (blue curve) was investigated in our previous work [23] and was found to be caused by the transient recapture of an electron that is transferred from one argon atom to the other, i.e. by the laser-induced transfer of electron (LITE) mechanism.

In the present work we are interested in the origins of the much smaller CEP-shift of \( A_{v,1,2} \) between the channels \( \text{Ar}(2,2) \) and \( \text{Ar}(1,2) \). Because both channels start with the emission of two electrons from each argon atom, one is tempted to assume that the CEP-shift is due to the electron recapture process that is present for the \( \text{Ar}(1,2) \) but not for the \( \text{Ar}(2,2) \) channel. However, as we will show below, in detail the situation is much more complicated.

Given the small CEP-shift between the \( \text{Ar}(2,2) \) and \( \text{Ar}(1,2) \) channels and the relatively low event numbers in the \( \text{Ar}(1,2) \) channel, we have performed a thorough statistical analysis to corroborate the significance of this small CEP-shift and to obtain its value. The measured distributions of \( p_{Z_{e}} = -p_{R} \) for the two channels, from which the corresponding asymmetry parameters \( A_{v} \) are obtained, contain about \( 2.70 \times 10^{5} \) and \( 3.90 \times 10^{5} \) events for the channels \( \text{Ar}(1,2) \) and \( \text{Ar}(2,2) \), respectively. These distributions are divided into 30 bins for the CEP-range 0 to \( 2\pi \). For each of the 30 bins filled with about 890 respectively 1.30 \times 10^{4} \) events, we calculated, assuming normal distribution, the mean value of the \( A_{v} \) value and the statistical \( \pm 1 \sigma \) error bar. These are the data shown in figure 1(b). The data were then fitted by sinusoidal functions \( f(\varphi_{\text{CEP}}) = A \sin(\omega \varphi_{\text{CEP}} + \varphi_{0}) + f_{0} \) with a fixed periodicity of \( \omega = 2\pi \) using the Levenberg–Marquardt algorithm, taking into account the statistical error bars. The \( \pm 1 \sigma \) confidence interval of \( \varphi_{0} \) for the \( \text{Ar}(1,2) \) channel is indicated in figure 1(b) by a green shaded area around the curve. For the other channels shown in the figure this confidence interval is smaller than the width of the lines. To quantify the value of the CEP-shift between the \( \text{Ar}(2,2) \) and \( \text{Ar}(1,2) \) channels, we used Welch’s t-test, testing for the hypothesis that the difference of \( \varphi_{0,1} - \varphi_{0,2} > \Delta \), where \( \Delta \) is a certain test-value of the experimentally observed CEP-shift between the two channels \( \text{Ar}(1,2) \) and \( \text{Ar}(2,2) \) which we have denoted here for the sake of brevity by 1 and 2, respectively. For a significance level of 0.05 and the number of events and bins given above we obtain that the maximum CEP-shift \( \Delta \) that still fulfills the test-hypothesis \( (p \text{-value} 0.0499) \) is 11.25° equivalent to 0.063 \( \pi \) rad.

3. Simulations

To gain insight into the field-driven electron dynamics underlying the experimentally observed CEP-shift between the \( A_{v} \)-curves of the \( \text{Ar}(1,2) \) and the \( \text{Ar}(2,2) \) channels depicted in figure 1(b), we performed 3D classical ensemble model calculations [56, 57]. This numerical model incorporates the interaction between electrons and nuclei in the intense laser field using Newton’s classical equations and allows tracing their trajectories during and after the laser pulse. Even though classical trajectory models neglect all quantum effects such as pathway interferences, it is known that they are reliable in reproducing experimental observables on a qualitative level. For example, classical trajectory models were used to successfully explain photoelectron distributions from two-color fields [58, 59], the sub-cycle ionization dynamics in circularly polarized fields [60, 61], and even the complicated process of electron–electron correlation involved in recollision-induced double ionization in linearly polarized fields [62] and two-dimensional two-color waveforms [63, 64]. In problems directly related to the present work classical trajectory models could well reproduce the angular distributions of fragment ions emitted during strong-field ionization-fragmentation of the argon dimer [57], and they could explain the sensitivity of electron recapture processes via the FFI mechanism to the laser field’s waveform [44]. However, due to the neglect of quantum effects, certain quantities calculated with classical models, such as ionization or scattering cross sections, may differ from those obtained with quantum models.
Nevertheless, classical trajectory models are valuable tools to unveil the underlying mechanisms leading to experimental observables in complex multi-electron, multi-dimensional problems such as the present one.

In our experiments, the laser intensity is well above the over-the-barrier threshold [65, 66]. Therefore, the outermost electron is rapidly stripped from each atom of the argon dimer at the rising edge of the laser field and leaves the interaction region quickly. It is therefore reasonable to assume that the motion of the remaining electrons and ions is not affected by the first two emitted electrons [56]. In our model, we thus ignore the influence of the first electron in each argon atom and thus the starting configuration of the dimer for the simulation is $\text{Ar}_2^{2+} = (\text{Ar}^{2+} + e^-) + (\text{Ar}^{2+} + e^-)$, i.e., two doubly charged argon ion potentials separated by $R_{\text{eq}}$ with an active electron bound to each of them. This approach has previously been used successfully to model the strong field fragmentation dynamics of argon dimers and trimers [56, 57]. The error in the CEP-dependence of the electron emission asymmetry that might result from the neglect of the first two ionization steps is expected to be small, since the two electrons are emitted early in the pulse when the laser vector potential is still small.

To reflect the situation in the experiment, the orientation of the dimer with respect to the laser polarization axis is arbitrary and the initial conditions of the two electrons are randomly selected from a microcanonical distribution around their parent nuclei with a binding energy equal to the double ionization potential of the argon dimer. This initial configuration is subject to a laser electric field of form $E(t) = -E_0 \exp(-4 \ln(2) (t/2T)^2) \cos(\omega t - \varphi_{\text{CEP}}) \hat{e}_z$, where $E_0$ is the peak laser field, $\omega$ the laser angular frequency, $\varphi_{\text{CEP}}$ the CEP, $T = 2\pi/\omega$ and $\hat{e}_z$ is the unit vector along the laser polarization direction $z$. The motion of the electrons and argon atoms under this laser electric field is governed by classical Newton’s equations of motion and continues to evolve after the conclusion of the laser pulse for a duration of 500 laser cycles to ensure a complete fragmentation of the argon dimer.

Then, the fragmentation channel is identified by an energy criterion of the final simulation state. For $\text{Ar}(1,2)$ a single and for $\text{Ar}(2,2)$ both electrons are required to have an energy larger than zero. To qualify as $\text{Ar}(1,2)$, one electron must have an energy larger than zero and additionally the KER of the fragmentation has to be between 12 eV and 18 eV, which is the experimentally determined KER range of the $\text{Ar}(1,2)$ channel, cf figure 1(a). The simulated CEP-dependence of $A_t$ for the three channels of interest is depicted in figure 1(c). As can be seen, the amplitude of the $A_t$-modulation is significantly larger in the simulated data than in the experimental one. This is a consequence of the neglect of quantum effects in the model, as discussed above, and possibly also of treating the ions as point charges. As a consequence, the simulated electron momentum distributions are somewhat narrower than the measured ones [23], translating into larger asymmetry values. However, figure 1(b) shows that the simulated CEP-dependence of $A_t$ is very similar to the measured curves for all three channels of interest. In particular, the right phase shift between the $\text{Ar}(1^*,2)$ and $\text{Ar}(2,2)$ channels observed in the experiment is well reproduced, albeit with a slightly larger value of about 0.1\pi. As mentioned above, the CEP-shift between the $\text{Ar}(1,2)$ and $\text{Ar}(2,2)$ channels is due to the LITE process that leads to a time delay for the ionization of the second electron [23]. The origin of the much smaller CEP-shift between the $\text{Ar}(1^*,2)$ and $\text{Ar}(2,2)$ channels will be discussed in the following.

4. Discussion

To obtain insight into the experimentally observed CEP-shift between the $\text{Ar}(1^*,2)$ and $\text{Ar}(2,2)$ channels we use our numerical model. It has been shown previously that in about 80% of all cases Rydberg states in argon dimers are populated by electron recapture via the FFI mechanism rather than by resonant excitation [36–38]. An analysis of the electron trajectories simulated using our model confirms this value. Hence, the CEP-shift between the $\text{Ar}(1^*,2)$ and $\text{Ar}(2,2)$ channels is dominantly caused by differences in the motion of the field-driven electrons rather than absorption and emission processes. To reveal these differences we used the 3D classical trajectory model described above to simulate the field-driven two-electron emission dynamics $\text{Ar}^+ \rightarrow \text{Ar}^+ \rightarrow \text{Ar}^{2+} + 2e$ for the $\text{Ar}(2,2)$, and the two-electron emission dynamics with the subsequent recapture process $\text{Ar}^+ \rightarrow \text{Ar}^{2+} - \text{Ar}^{2+} + 2e \rightarrow \text{Ar}^{2+} - \text{Ar}^{2+} + e$ for the $\text{Ar}(1^*,2)$ channel, respectively. A typical electron trajectory in space and energy over time leading to channel $\text{Ar}(1^*,2)$ as predicted by our model is shown in figures 2(a) and (b), respectively. The corresponding figures for a typical trajectory that leads to the $\text{Ar}(2,2)$ channel can be found in reference [23].

For a statistical analysis of the about $10^6$, $6 \times 10^3$ and $7.5 \times 10^5$ trajectories in the $\text{Ar}(1,2)$, $\text{Ar}(1^*,2)$ and $\text{Ar}(2,2)$ channels, respectively, that were propagated in our simulations we defined decisive instants that characterize each trajectory. For the trajectories of the two electrons in the $\text{Ar}(2,2)$ channel these are $t_{1\text{st}}$ and $t_{2\text{nd}} > t_{1\text{st}}$, which are the instants when the two electrons become emitted. These instants are defined by the criterion that the energies of the respective trajectories exceed the binding energy of their parent argon cation for the first time. For the trajectories of the two electrons in the $\text{Ar}(1^*,2)$ channel the situation is somewhat complicated by the fact that one of the two electrons is not only emitted but becomes recaptured sometime after its emission. Thus, it necessitates two instants, $t_{\text{Ryd}}$ and $t_{\text{Rec}}$, to characterize this recaptured trajectory. The first instant, $t_{\text{Ryd}}$, marks the moment of the emission of this trajectory, defined by the same energy criterion as in the other channel. The second instant, $t_{\text{Rec}}$, marks the moment when the trajectory becomes recaptured, defined as the instant when the energy of the trajectory changes from positive to negative and stays negative until the end of the simulation long after the laser pulse has passed. To characterize the other, non-recaptured trajectory in the $\text{Ar}(1^*,2)$ channel it is sufficient to only define its time of emission, $t_{\text{free}}$, by the same energy criterion as all the other emission times. The instants for the $\text{Ar}(1^*,2)$ channel are marked in figures 2(a) and (b).
The distributions of these decisive instants, separated for events with a positive or negative electron sum momentum along the laser polarization direction \( z \), \( p_{z \perp >0} \), are shown in figure 3 for CEP-values of 0\( \pi \), 0.3\( \pi \) and 0.5\( \pi \), respectively. For a first intuitive assessment of the simulated emission time distributions it seems helpful to compare them to distributions that would be expected if the ionic potential, in particular that of the neighboring ion, had no influence on the electron emission dynamics. In that case, the emission time distributions would be solely dictated by the shape of the laser electric field respectively the laser vector potential. For a strong field such that \( E(t) \approx 3 \times 10^{15} \text{ V/cm} \), the electron trajectories would be expected if the ionic potential, in particular that of the neighboring argon ion, was absent. This means that the non-recaptured electrons \( t_{\text{free}} \) should peak at the peaks of the laser electric field. Indeed, the red-colored distributions of \( t_{\text{free}} \) (first row, channel Ar\( ^{1+},2 \)) and \( t_{\text{1st}} \) (second row, channel Ar\( ^{2+},2 \)) roughly follow this simple picture. However, on closer inspection, the distributions also markedly deviate from that expected for a purely field-driven electron dynamics: the negative and positive areas are not equally distributed within a laser half cycle, they feature irregular shapes, and there also exist small peaks in between the main peaks. Thus, the binding potential of the dimer obviously crucially influences the trajectories of the emitted electrons.

To elucidate the details of the influence of the dimer potential on the electron emission dynamics and to understand the shapes of the \( t_{\text{free}} \) and \( t_{\text{1st}} \) distributions, we performed an in-depth statistical trajectory analysis for the Ar\( ^{1+},2 \) channel. A similar analysis was performed for the Ar\( ^{2+},2 \) channel in reference [23]. The results of the analysis for the Ar\( ^{1+},2 \) channel are summarized in figure 4. The green data points in this figure correspond to the recaptured trajectories and will be discussed below. For now we are only concerned with the red data points that correspond to the red-shaded \( t_{\text{free}} \) distributions of the trajectories that become free after the laser pulse, shown in the upper row of figure 3. Figure 4(a) depicts for these trajectories the distribution of their minimum distance, \( D_{\text{min}} \), to the neighboring argon ion. Two peaks can be observed, one centered at a small minimum distance \( D_{\text{min}} \approx 0.5 \text{ a.u.} \) and another one at a much larger value of \( D_{\text{min}} \approx 6 \text{ a.u.} \). The latter peak corresponds to trajectories that keep a relatively large distance to the neighboring argon ion on their way to the detector and do not interact with the neighboring ion, such as the red trajectory displayed in figure 2. The trajectories that form the peak at small \( D_{\text{min}} \) are detected within the time span of about 0.5 laser cycles and are emitted only during the next laser half cycle around the peak of the field. Thus, we find that a substantial fraction of the trajectories in the peak \( D_{\text{min}} < 2 \text{ a.u.} \) in figure 4(a) undergo the LITE process [23], in which an electron is transferred by a strong laser field across system boundaries, in the present case from one argon ion to the other, where it becomes transiently captured by the Coulomb potential of the distant entity. This means that the non-recaptured electrons in the Ar\( ^{1+},2 \) channel behave very similar to the first emitted electrons in the Ar\( ^{2+},2 \) channel. Also for those electrons we found in reference [23] that their majority is emitted by field-ionization and a fraction undergoes the LITE process before emission. This explains the similarity of the \( t_{\text{free}} \) and \( t_{\text{1st}} \) distributions in figure 3. Because the emission direction of trajectories that become transiently trapped is strongly determined by the ion’s Coulomb field and is not directly related to the sign of the laser vector potential at the time of emission, it are these
Figure 3. (a)–(c) Simulated electron emission time distributions in the Ar(1∗,2) channel for CEP-values of 0π, 0.3π and 0.5π. (d)–(f) Same as upper row but for the Ar(2,2) channel. The emission times of the two electrons in the Ar(1∗,2) channel (t_free and t_Ryd) and the two electrons in the Ar(2,2) channel (t_1st, t_2nd) are defined in figure 2 and in the text. The upper (lower) half in each figure shows the emission time distributions where the sum momentum of the two emitted electrons, p_{Σ,e}, is positive (negative).

Figure 4. (a) Distributions of the minimum distance D_{min} to the neighboring ion of each trajectory emitted in the Ar(1∗,2) channel for ϕ_{CEP} = 0. The distributions are separated into recaptured (green) and not recaptured trajectories (red). (b) The distributions of the time intervals Δt that the trajectories from (a) stay in a small region D < 3.6 a.u. around the neighboring ion.

trajectories that cause the deviations of the t_free and t_1st distributions in figure 3 from a pattern that would be expected if the dimer’s binding potential had no influence on the emitted electrons. In addition, also the directly emitted trajectories that circle around the neighboring ion, such as the red example trajectory in figure 2, lead to the deviations of the t_free and t_1st distributions from regular double peak structures. All in all this explains their shapes in figure 3.

Now we turn to the distributions of the instants t_Ryd, green colored in figures 3(a)–(c). These are the emission instants of the trajectories that undergo FFI and become recaptured in Rydberg states after the laser pulse. Their green D_{min} distribution in figure 4(a) shows that the absolute majority of all recaptured trajectories approach the neighboring argon ion very closely. And the corresponding Δt distribution in figure 4(b) shows that from these trajectories again the absolute majority becomes transiently trapped in the Coulomb field of the neighboring argon ion by about 0.4 laser cycles and, thus, are emitted only during the next laser half cycle. That is, we find that almost all of the recaptured trajectories undergo the LITE process before their emission and subsequent recapture to a Rydberg state.

Thus, it seems that the LITE mechanism and the transient trapping on the neighboring ion following this process, leads to a higher chance for FFI. Even though we cannot substantiate this speculation with our data, a plausible reason for this behavior could be that the delay in emission of the transiently trapped trajectories after LITE causes that these trajectories are emitted into the field only when the laser pulse already starts to fade. As a consequence, these trajectories are not driven away from the argon dimer very far and also do not reach very high kinetic energy. Therefore, their recapture probability might be enhanced as compared to trajectories emitted earlier at higher field strength. The green-colored recaptured trajectory in figure 2 exemplifies this behavior.

As we have shown in reference [23], also almost all of the second emitted electrons in the Ar(2,2) channel undergo the LITE process before emission. This is reflected in the t_2nd distributions in figures 3(d)–(f), as the emission direction of the corresponding trajectories does not consistently follow the laser vector potential because of the strong influence of the ionic Coulomb potential on the transiently trapped trajectories, as mentioned above. Also, the t_2nd distributions peak close to the field maxima, which reflects the fact that the transiently trapped trajectories are relatively weakly bound. However, even though both the recaptured trajectories in the Ar(1∗,2) channel and the second emitted electrons in the Ar(2,2) channel are subject to LITE before emission, the
dependence of electron emission that is similar for the
The shapes and positions of the shift it is necessary, as we will show, to also consider the consequences of these differences will be the content of the following section.

4.2. CEP-dependence of $\mathcal{A}_c$ and CEP-shift between $\text{Ar}(1^+,2)$ and $\text{Ar}(2,2)$ channels

With the help of the emission-time distributions in figure 3 the measured CEP-dependence of $\mathcal{A}_c$ shown in figure 1(b), can be elucidated. The measured $\mathcal{A}_c$ over CEP of the Ar(2,2) and Ar(1⁺,2) channels are separated by only about 0.1π and thus exhibit similar CEP-dependence. They show both negative extremal values for small values of the CEP around $\varphi_{\text{CEP}} = 0\pi$, and increase with increasing CEP to positive maxima around $\varphi_{\text{CEP}} = 0.8\pi$. The emission time distributions in figure 3 explain this trend: as the CEP increases, all distributions change from being dominated by peaks pointing into $P_{\text{max}} < 0$ ($\mathcal{A}_c < 0$) at $\varphi_{\text{CEP}} = 0\pi$, via roughly balanced distributions ($\mathcal{A}_c \approx 0$) at $\varphi_{\text{CEP}} = 0.3\pi$, to being dominated by distributions pointing into $P_{\text{max}} > 0$ ($\mathcal{A}_c > 0$) at $\varphi_{\text{CEP}} = 0.5\pi$. Thus, the measured large-scale CEP-dependence of electron emission that is similar for the Ar(2,2) and Ar(1⁺,2) channels (except for their small offset of about 0.1π), although partly determined by complex electron transfer and transient recapture processes, can be precisely understood based on the sub-cycle ionization timing revealed through our simulations.

To explain the small CEP-shift between the Ar(2,2) and Ar(1⁺,2) channels it is, however, not sufficient to only regard the overall, integrated positive or negative directionality of the electron emission peaks. In order to understand the CEP-shift it is necessary, as we will show, to also consider the precise positions and even the shapes of the emission peaks. The shapes and positions of the $t_{\text{free}}$ and $t_{\text{Ryd}}$ distributions in the Ar(2,2) respectively Ar(1⁺,2) channels are quite similar, cf figure 3. Thus, they alone cannot account for the observed CEP shift between these two channels. More prominent differences, though, can be noticed between the emission distributions of the other electrons released in each channel, i.e., between the $t_{\text{Ryd}}$ and $t_{\text{free}}$ distributions.

As can be clearly seen, the $t_{\text{Ryd}}$ distributions of the recaptured electrons in the Ar(1⁺,2) channel are much narrower than the $t_{\text{free}}$ distributions in the Ar(2,2) channel. This is due to the fact that the recapture of the electron in a Rydberg state requires that it returns to the nucleus with almost zero momentum. When the force due to the laser electric field dominates the electron motion, this imposes onto the electron the requirement that it is emitted within a narrow time-range around the maxima of the electric field. This can be understood from the relation $\mathbf{p}_t = -\mathbf{A}(t)$. To reach negligible momentum $|\mathbf{p}_t| \approx 0$ upon conclusion of the laser pulse this relation dictates that the electron emission times $t = t_{\text{Ryd}}$ are confined to narrow ranges around the zeros of the laser vector potential $\mathbf{A}(t)$ or, equivalently, the maxima of the laser electric field $\mathbf{E}(t)$. In reality, the influence of the ionic Coulomb field leads to a small shift of the narrow emission time distributions away from the field’s maxima [71, 72]. Both, the narrow shape and small shift are clearly visible in the $t_{\text{Ryd}}$ distributions in figure 3.

In comparison with the $t_{\text{Ryd}}$ distributions, the $t_{\text{free}}$ distributions in the Ar(2,2) channel are significantly broader. That is because in contrast to the emission of the recaptured electrons, this ionization step is subject to no specific timing constraints. As a result, the emissions of these transiently captured (due to LITE, as explained above) and therefore relatively weakly bound trajectories take place dominantly by field ionization. Thus, the corresponding emission time distributions peak close to the field maxima, cf figures 3(d)–(f).

As shown in figure 1, the sign of the CEP-shift is such that at any given value of $\varphi_{\text{CEP}}$ within the range $\varphi_{\text{CEP}} = [0, 0.8\pi]$ the $\mathcal{A}_c$-value of the Ar(2,2) channel is always more positive than that of the Ar(1⁺,2) channel. The opposite is true for $\varphi_{\text{CEP}} = [0.9\pi, 1.7\pi]$. Thus, in the CEP-range $\varphi_{\text{CEP}} = [0, 0.8\pi]$ that is covered by the three values 0, 0.3π and 0.5π depicted in figure 3, the mean sum momentum of the emitted electrons along $z$, $P_{\text{sum},z}$ must always be more positive for the Ar(2,2) channel than for the Ar(1⁺,2) channel. Obviously, the broader shape of the time distributions in combination with the small Coulomb-induced delay to the laser field maxima of the much narrower $t_{\text{Ryd}}$ distributions cause that overall the second emitted electrons in the Ar(2,2) channel have a slightly higher chance to be emitted at instants that favor a positive electron momentum than the recaptured electron in the Ar(1⁺,2) channel, which explains the small relative CEP-shift between the $\mathcal{A}_c$ curves of the Ar(1⁺,2) and Ar(2,2) channels.

4.3. Electron recapture and localization

Our study of the origins of the CEP-dependent electron emission in the Ar(1⁺,2) channel has revealed unprecedented insight into the electron recapture dynamics on sub-cycle times. Astonishingly, as we showed, of the two emitted electrons in this channel, it is the recaptured rather than the directly emitted one that is transiently transferred across the system boundary to the other argon ion. Paired with the mere fact that the recapture process is amenable to the shape of the laser field at all, this raises hopes for the possibility to implement laser field control of molecular reactions initiated by strong field-driven donor-acceptor electron transfer processes. In the following we will discuss to what extent our present implementation comes close to this vision, and how future work could mitigate certain shortcomings of our approach.

One of the two key processes investigated by our study is the electron recapture process through FFI, which results in a highly excited argon ion after the laser pulse. In molecules, the population of a (highly) excited electronic state is an important mechanism for inducing molecular reactions such as dissociation. The outcome of such reactions crucially depends on the energy of the populated excited state. Our simulations reveal that in our experiment mostly loosely bound Rydberg states with a mean binding energy of 0.025 a.u., which corresponds to a principal quantum number of $n \approx 8$, are populated, see figure 5. This is in good agreement with previous
experimental and theoretical studies on the atomic [33, 43, 44, 46, 71] as well as the argon dimer case [36].

The population of a weakly bound Rydberg state can open up a number of molecular reactions, including dissociation, fragmentation and the generation of radicals [24–28]. However, in quantum control it is preferred that a specific reaction is triggered, which usually means that more strongly bound electronic states should be populated [53, 73–76]. However, as in FFI a slow electron is recaptured by an ion’s Coulomb potential, this process by its nature prefers weakly bound states. Nevertheless, we showed in reference [43] that states down to \( n = 5 \) are populated by FFI. Such states are highly relevant for molecular dissociation reactions [25–27].

Yet, FFI leads to the population of bound states with a broad energy spectrum. It is, thus, important to harness the FFI process such that preferentially more strongly bound states with a narrower spectrum are populated. One possibility for this seems to be two-dimensional laser waveforms composed of two colors, e.g., OTF fields [77–79] or counter-rotating circular twocolor fields [64, 80, 81]. With such waveforms not only the emission and recollision timing of recaptured electrons can be controlled, as in the present work using the CEP of few-cycle pulses, but also the trajectory of the recolliding electron within the laser polarization plane. We could previously show that for Rydberg electrons the use of OTF fields opens up control over the properties of their Kepler orbits such as their angular momentum, direction and shape [44]. It seems, therefore, possible that carefully designed two-dimensional waveforms can also be used to influence the energy spectrum of recaptured electrons.

The second key process investigated in the present work is the electron transfer through the LITE mechanism. We have shown above that almost all of the recaptured electrons first undergo this transfer process to the neighboring argon ion where they become transiently trapped and are emitted by field-ionization only up to almost a laser half cycle later. To understand whether this transfer and transient trapping step influences the recapture process, we divided all computed electron trajectories into events where the Rydberg electron has localized at its parent ion or the neighboring ion after the two ions have become well separated at the end of the simulation run. An example trajectory that visualizes the recapture of the electron at its parent ion during fragmentation of the argon dimer into two \( \text{Ar}^2^+ \) ions is depicted in figures 6(a) and (b). The other case, recapture on the neighboring ion, is visualized in figures 6(c) and (d). The left figure panels (figures 6(a) and (c)) show the trajectories during and shortly after the laser pulse, the right panels (figures 6(b) and (d)) long after the laser pulse.

It can be seen that upon conclusion of the pulse the electron is in both cases already recaptured in a Rydberg orbit. Because the two argon ions are moving much slower than the electrons, at that time their distance is still small (close to the equilibrium distance) and the Rydberg orbit cannot be assigned to either of the two argon nuclei. Only much later, as the distance of the two argon ions increases due to Coulomb explosion, the electron finally localizes at either of the two (figures 6(b) and (d)). Thus the localization process is temporally well separated from both the recapture process and the transfer process through LITE. Furthermore, our simulations reveal that both
cases, recapture on the parent ion or on the neighboring ion, take place almost equally likely. That means, in our experiment the localization of the Rydberg electron is a statistical process. This is understandable since for a symmetric dimer with two charge ions of the same charge state both ions exert the same attractive force on the electron that orbits around both ions. The situation is different for dimers where the two ions exhibit different charge states. In that case the electron localizes more likely on the ion with the higher charge due to its higher attractive force [38, 42]. Therefore, it will be interesting to investigate the sub-cycle electron dynamics leading to electron recapture in asymmetric channels and its dependence on the shape of the laser field in asymmetric channels, particularly for molecular dimers, where the molecules can also dissociate.

Because the Rydberg electron localization takes place long after the laser pulse, also the CEP of the laser pulses is irrelevant for the localization process. This is confirmed by figure 6(e) which depicts $A_z$ as a function of the CEP separated into the events where the recaptured electron localizes on its parent argon ion and the neighboring ion. Both curves agree with each other and with the combined $A_z$ curve reproduced from figure 1(c), confirming the independence of the localization process from the CEP. As a consequence, we conclude that the measured CEP-dependence of the parameter $A_z$ in the Ar(1*,2) channel shown in figure 1(b) is entirely due to electron emission by field-ionization, the electron transfer by LITE and the recapture process due to FFI but not due to the Rydberg electron localization on the ions. Influence of the localization process by the laser field shape might be possible with the two-dimensional waveforms mentioned above. This is motivated by the fact that they can determine the properties of the Rydberg orbits [44] and therewith cause some preponderance for localization on one of the two ions in the dimer. Additionally, a narrower and deeper lying energy spectrum of the recaptured electron that might be possible with these laser waveforms would also be beneficial for control over the localization process.

5. Conclusion

In conclusion, we have investigated electron recapture processes in argon dimers driven by intense few-cycle laser pulses with a known CEP. Our main motivation was to obtain insight into the sub-cycle laser field-driven electron dynamics that underlie the electron recapture process responsible for the frustrated field-ionization (FFI). To this end we compared the CEP-dependence of the mean electron sum momentum of all emitted electrons in two ionization-fragmentation channels, Ar(1*,2) and Ar(2,2). In both channels two electrons are emitted from each argon ion, but in the Ar(1*,2) channel one of them is recaptured by the Coulomb potential of the argon ions.

In our experiments we found a distinct CEP-dependence of the electron emission asymmetry for both channels, and a small relative CEP-shift between the two channels. With the help of a classical ensemble trajectory model we could explain that almost all of the later recaptured electron trajectories in the Ar(1*,2) channel are initially transferred to the neighboring argon ion by the LITE-process where they are transiently captured. Subsequently, after up to roughly half a laser cycle, they are emitted by field-ionization and finally, upon conclusion of the laser pulse, they are recaptured in a Rydberg state. Thus, the electron emission step is very similar to the Ar(2,2) channel for which a similar emission behavior was found [23]. The small relative CEP-shift between the channels arises through a subtle difference in the emission timing caused by the momentum restrictions of the recaptured electrons which dictate that these electrons, in contrast to the non-recaptured electrons, exhibit near-zero momentum upon conclusion of the laser pulse.

The CEP-dependence of the electron transfer process that was identified as a key step in the population of highly excited states in the Ar(1*,2) channel could indicate that laser field control of molecular reactions on a distant entity initiated by strong field-driven donor–acceptor electron transfer processes might become possible. Our simulations show that the electron is recaptured to Rydberg states with a mean principal quantum number $n \approx 8$. Its orbit surrounds both ions in the argon dimer. Upon the slow separation of the two argon ions due to the repulsive Coulomb force, which takes place mainly after the pulse, the electron statistically localizes on one of the two ions with roughly equal probability. Thus, control over the sub-cycle electron emission timing and the recapture process, as demonstrated here using the CEP of few-cycle pulses, is not sufficient to also determine the electron localization necessary to determine a reaction on the distant entity. Such localization control may, however, be possible using two-dimensional laser waveforms, e.g., with OTC fields [77–79], for which we could previously show that they can influence the shape, direction and angular momentum of the Rydberg orbits populated by the electron recapture process [44].

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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