Coherent Electronic Wave Packet Motion in C_{60} Controlled by the Waveform and Polarization of Few-Cycle Laser Fields


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Strong laser fields can be used to trigger an ultrafast molecular response that involves electronic excitation and ionization dynamics. Here, we report on the experimental control of the spatial localization of the electronic excitation in the C_{60} fullerene exerted by an intense few-cycle (4 fs) pulse at 720 nm. The control is achieved by tailoring the carrier-envelope phase and the polarization of the laser pulse. We find that the maxima and minima of the photoemission-asymmetry parameter along the laser-polarization axis are synchronized with the localization of the coherent electronic wave packet at around the time of ionization.

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Electrons determine the forces on the nuclei in molecules. Tuning the nonequilibrium electronic dynamics before the onset of significant nuclear motion opens new routes for tailoring chemical reactivity. For few-cycle optical pulses, varying the phase between the envelope and the field amplitude [carrier-envelope phase (CEP)] can be used to control electronic dynamics induced in molecules during the interaction with the pulse [1–3]. Electronic dynamics are typically probed indirectly by recording molecular fragmentation patterns of dissociative (ionization) channels exploiting the coupling between the electronic and nuclear degrees of freedom [4–26]. The analysis of the fragmentation patterns is usually complex—even for simple diatomic molecules—and quickly becomes prohibitively complicated for large polyatomic molecules because of the large number of fragmentation channels [3]. Angularly resolved photoionization by ultrashort laser pulses has been advocated for probing the electronic dynamics before the onset of significant nuclear motion (see, e.g., [27–31]).

Fullerenes are nanometer-size systems with interesting physical properties, including high polarizability [32], superatomic molecular orbitals [33,34] with macroatom behavior [35], large photoionization cross sections [36,37], and efficient high-harmonic generation [38–40]. The ionization and fragmentation of C_{60} have been investigated extensively in the past (see, e.g., [35,41–47]). C_{60} is very stable and is one of the few molecular systems for which the ionization energy is smaller than the lowest fragmentation threshold. Therefore it is an ideal system for probing electronic dynamics, and, when suitably excited, the electronic density oscillates on a nanometer scale. Moreover, in the experiments reported here, the pulse duration is short enough to avoid significant thermionic emission that occurs for longer pulse durations of hundreds of femtoseconds to nanoseconds [48,49]. In this Letter, we demonstrate the control over transient electronic dynamics in a large polyatomic system, the C_{60} fullerene, and we find that the angular distribution of direct photoelectrons reflects the spatial localization of the electronic wave packet at about the time of ionization.

The electron emission from C_{60} as a function of the CEP is recorded with phase-tagged velocity-map imaging (VMI) [50]. Details of the experimental setup are contained in the Supplemental Material [51]. The few-cycle laser pulses are focused into the VMI chamber where they intersect a molecular beam of C_{60} powder in a home-built oven. Measured 2D-momentum images correspond to projections along the spectrometer axis (p_{yz}). Linear polarized (LP) pulses are polarized along the y axis and circular polarized (CP) pulses in the yz plane. The CEP is measured by a single-shot phase meter [65,66] and the absolute CEP was determined from Xe reference scans.
Quantum dynamical (QD) and classical Monte Carlo (MC) trajectory simulations were used to theoretically investigate the CEP-dependent electron emission from C$_{60}$. Both calculation methods are described in the Supplemental Material [51] and briefly in the following. In our QD simulations, the photoionization and photoexcitation electronic dynamics induced by a short laser pulse are computed by numerically solving the time-dependent Schrödinger equation using a coupled equation scheme including bound and ionized states. The bound states are described in a basis of 407 electronic states of C$_{60}$ (i.e., all states below the ionization threshold). The acceleration and deceleration of the continuum electron by the electric field, and thus the scattering dynamics, are accounted for. The angular distribution of a continuum electron with a given momentum depends on the coherently excited bound states at the instant of ionization and their coupling to the continuum. Thus, by varying the polarization and the CEP of the pulse, the time-dependent wave packet evolves differently, which is reflected in the angular distribution of the photoelectrons [30,31,67–69]. The electron spectra are computed by integrating the population of the ionized states at the end of the pulse. The calculations have been focal-volume averaged (in the two dimensions perpendicular to the laser propagation) for comparison to the experimental data.

We complement our QD calculations with MC simulations of electron emission and rescattering in analogy to the simple man’s model [70]. Such simulations have been successfully used for the description of electron emission and rescattering for atoms for both LP [71,72] and CP [73,74] and have been generalized to electron emission from nanoparticles [75] and from metal nanostructures [76,77].

Experimentally obtained CEP-integrated electron momentum images for LP and CP at the same laser field amplitude of 22.1 GV m$^{-1}$ corresponding to a cycle-averaged peak intensity of $6.5 \times 10^{13}$ W cm$^{-2}$ and $1.3 \times 10^{14}$ W cm$^{-2}$, respectively, are shown in Figs. 1(a)–1(c). Figures 1(d) and 1(e) show the computed and experimental ionization yield as a function of the radial momentum $p_r$, defined as $p_r = \sqrt{p_x^2 + p_y^2}$. Contributions from both direct and rescattered electrons can be distinguished by the MC simulations. For LP, rescattered electrons dominate the signal above $p_r = 0.6$ a.u. For CP, the rescattered electrons only start to dominate the total signal around 1.3 a.u. The high-momentum cutoff, corresponding to an energy of about $10U_p$, where $U_p$ is the ponderomotive potential, is in both cases around 1.5 a.u. The QD-simulated photoelectron spectra diverge from the measured data in the low-momentum region. This is due to the fact that the Coulomb interaction between the ionized electron and the cationic core is not well represented due to our use of a plane wave basis to describe the continuum electron, which leads to a lower photoelectron yield at low momenta. At very low kinetic energies the QD simulations underestimate the contribution of ionization from deeply bound states, which are, however, quickly depopulated within the pulse.

In Figs. 2(a) and 2(b) we show the amplitude and phase of the CEP-dependent electron yield for LP and CP. In order to obtain the graphs, we integrated the CEP-dependent yields over $p_x$, $p_y$ using 0.02 a.u. $\times$ 0.02 a.u. bins. The integrated yields are parameterized as a sinusoidal $N(\phi') = N_0 \sin(\phi + \phi_0)$, where $N_0$ is the amplitude and $\phi_0$ denotes a phase offset. The parameters $N_0$ and $\phi_0$ are shown as a function of $p_x$ and $p_y$ in Figs. 2(a) and 2(b). A CEP-dependent yield with a nearly constant amplitude and phase for the highest discernible direct electrons is found within the range of momenta marked by a solid red line. This range is contained within an angle of about $\pm 15\degree$ along the polarization axis. For the same angular range, the region of the rescattering electrons close to the cutoff is marked by a solid black line.

The CEP and momentum dependence of the directional electron emission from C$_{60}$ for both LP and CP are analyzed via the asymmetry parameter, defined as

$$A(p, \phi) = \frac{N_{+y}(p, \phi) - N_{-y}(p, \phi)}{N_{+y}(p, \phi) + N_{-y}(p, \phi)}$$

where $p$ is the momentum vector of the continuum electron, $N_{+y}(p, \phi)$ and $N_{-y}(p, \phi)$ represent the yield of...
the continuum electrons in the +y and −y direction, respectively, and φ is the CEP. The asymmetry typically shows an oscillatory behavior with CEP [79]. A strong variation of the asymmetry parameter indicates a large degree of control, which results from the short, near-single cycle pulses. Integration of the momentum images over the angular ranges indicated in Figs. 2(a) and 2(b) yields the experimental asymmetry maps as a function of radial momentum and φ in Figs. 2(c) and 2(d), which we compare to the theoretical data in Figs. 2(e)–2(h).

For LP and CP [Figs. 2(c)–2(h)] characteristic differences can be discerned between low-momentum electrons ($p_r \leq 0.6$ a.u.) corresponding to direct ionization and high-momentum electrons ($p_r \geq 0.6$ a.u.) corresponding to rescattered electrons for LP. In the high-momentum region the predictions by both classical and quantum dynamical simulations agree well with the experimental data in periodicity and phase shifts with $p_r$. This is further supported by the comparison of the asymmetries integrated over a selected range of high momenta ($1.3 \leq p_r \leq 1.5$ a.u.), see Figs. 2(i) and 2(j). The amplitudes differ here by only about a factor of 2 between the results.

In contrast to the generally good agreement between experiment and theory at high momenta, for a band in the low-momentum region ($0.4 \leq p_r \leq 0.6$ a.u.), chosen to be at the highest discernible momenta for direct electrons in LP, the classical simulations exhibit a strong phase shift with respect to the experimental data for LP. This indicates that the direct electron emission is not accurately described within the MC simulations. In contrast, the QD simulations reproduce accurately the phase of the asymmetry and its magnitude semiquantitatively. Moreover, these simulations provide insights on the relation between the anisotropy and the bound-states dynamics. Our interpretation is as follows: The angular distribution of the photoelectrons and, therefore, the asymmetry parameter depends on the shape and localization of the transiently formed bound-state wave packet as well as its coupling to the continuum. While the photoionization coupling elements vary with the electron momentum (magnitude and direction) but are independent of the electric field strength, the bound-state wave packet dynamics strongly depend on the pulse characteristics such as the CEP, the strength of the electric field, and the polarization. The variation of the asymmetry parameter as a function of CEP for the direct ionization is thus controlled by the motion of the wave packet modulated by the momentum-dependent coupling elements.

The time-dependent electron densities for LP and CP obtained from the QD simulations are depicted in Fig. 3. The pulse induces complex transient dynamics resulting in collective electron motion. At the beginning of the pulse, the ground state is efficiently excited by multiphoton transitions to the higher states. When the electric field reaches its maximum, close to $t = 3.5$ fs, the ionization rate steeply increases [see Figs. 3(a) and 3(b)]. At each time, and depending on the value of the CEP, ionization from a different superposition of the ground state and transient excited states occurs, leading to a different angular distribution of the continuum electron.

The evolutions of the bound electron dynamics are reflected by the dipole moments, shown in Figs. 3(c) and 3(d) for LP and CP, respectively. They follow the electric field almost adiabatically at the beginning of the pulse, until ionization occurs. The excited states are accessed by multiphoton transitions. At the field maximum, the electronic states ionize and subsequently the dipole moment collapses. For $\phi = 0$, the electron density is mainly localized on the bottom of the molecule (in the -y direction) at $t = 3.5$ fs [Fig. 3(e)], when the photoionization probability is maximum since direct ionization is more probable where the electron density is the largest. For this CEP, the asymmetry parameter is negative for low ($< 0.6$ a.u.) momentum [see Fig. 2(i)], which corresponds to a preferential ionization of the electrons in the -y direction.
The leftward tilt is observed for electrons gaining high momenta ($p \gtrsim 1$ a.u.) in the CP laser field. For the latter to occur, the instantaneous momentum vector should stay aligned with the laser induced force $\mathbf{F}_{\text{N}}(t) = -\mathbf{F}(t)$ during the rescattering process (Fig. 4). This subset of trajectories involves electrons taking off from the tunneling exit towards the target and undergoing typically two to three small-angle collisions at atoms of the $C_{60}$ shell, thereby rotating the velocity vector in tune with the rotation of the CP laser field. The electrons eventually emerge with momentum vector $p_{\text{final}}$ pointing in the direction opposite to that of their initial position vector and that of the electric force vector $\mathbf{F}_{\text{N}}(t_{\text{tunnel}})$ at the tunnel exit. This 180° rotation differs from the 90° rotation between $\mathbf{F}_{\text{N}}(t_{\text{tunnel}})$ and $p_{\text{final}} = \int_{t_{\text{tunnel}}}^{\infty} \mathbf{F}_{\text{N}}(t) dt$ for circularly polarized light in the absence of rescattering. It is this advancement that leaves its mark as the leftward tilt in the asymmetry spectrum. The MC simulations indicate that about 1% of the trajectories lead to scattering and most of the electrons that reach high momenta undergo a sequence of small-angle rescatterings.

This particular recollision mechanism differs from the conventional laser-induced rescattering for atomic or diatomic molecules, where circular polarization strongly quenches electron (back)scattering. Backscattering with high energy gain via multiple small-angle collisions in elliptical or circular polarization will likely also play a role in other extended targets such as large molecules, clusters, nanoparticles, and droplets.

In conclusion, the polarization and the CEP of intense few-cycle laser pulses were used to demonstrate the spatiotemporal control of electronic wave packet motion in $C_{60}$. The CEP-dependent asymmetry of the electron emission at high momenta can be understood from simple classical arguments, where the influence of the vector potential on the trajectory of the continuum electron needs to be taken into account. Furthermore, the classical simulations indicate that the leftward tilt of the asymmetry of...
the rescattered electrons for CP is caused by a series of small-angle collisions with the C60 shell. At low momenta, direct ionization dominates, and from our QD simulations we infer that the asymmetry parameter reflects the localization of the coherently excited electron density at about the time of ionization. Similar trends are expected to be observed in other fullerenes under comparable laser conditions. Furthermore, the spatiotemporal control demonstrated here can be extended to other systems, such as clusters or nanoparticles, that undergo collective electron dynamics when exposed to a strong field.

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