

Attosecond probing and control of charge migration in carbon-chain molecule: Supplementary Material

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1. Experimental details

Our experimental setup is sketched in Fig. S1. The output of a commercial Ti: sapphire laser system (Astrella-USP-1K, Coherent, Inc.), which delivers 35 fs, 800 nm laser pulses at a repetition rate of 1 kHz, is split into two beams by a beam splitter (BS) for the nonadiabatic alignment of C₄H₂ molecules (the aligning laser, P₁) and the generation of harmonics (the driving laser, P₂). The aligning and driving pulses are parallel in the polarization. The time delay between these two pulses is adjusted by a motorized delay line installed in the arm of the aligning pulse. These two pulses are collinearly focused into a supersonic gas jet ejected from a nozzle (250 μ m diameter) with a backing pressure of 0.2 bars by a spherical mirror ($f=250$ mm). The gas jet is placed 2 mm after the laser focus to ensure good phase matching of the short-trajectory harmonics. The generated high harmonics are detected by a homemade flat-field soft x-ray spectrometer [1], which includes a 0.1-mm-wide, 15-mm-height entrance slit, a flat-field grating (1200 grooves mm⁻¹), and a microchannel plate (MCP) backed with a phosphor screen. A charge-coupled device (CCD) camera is used to record the harmonic spectral images.

In our experiment, we first measured HHG from C₄H₂ by using a one-color driving field. In this case, the driving laser P₂ is directly used to generate high-order harmonics. Figure

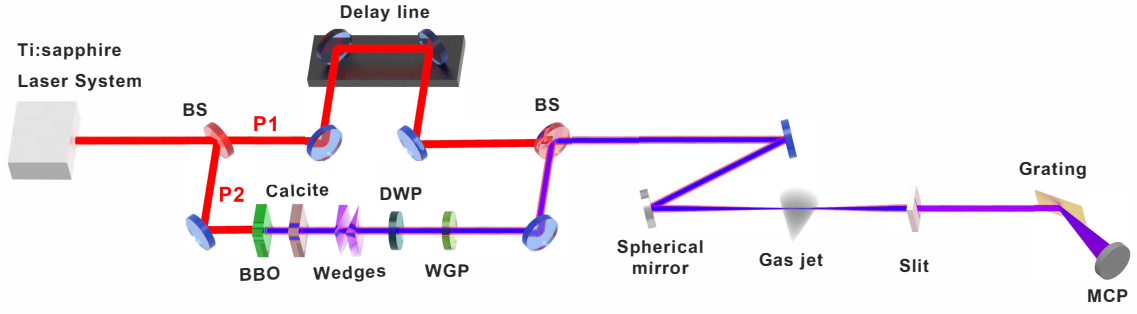


FIG. S1: Schematic diagram of the experimental set-up. BS: beam splitter, DWP: dual-wave plate, WGP: wire grid polarizer, MCP: microchannel plate.

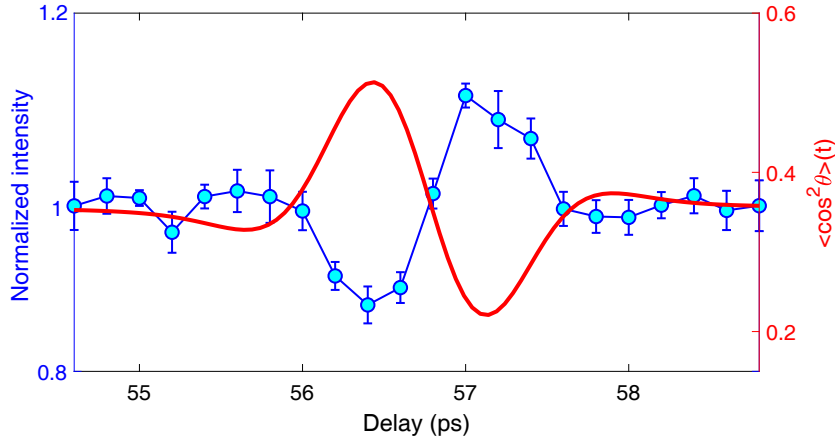


FIG. S2: HHG signals (circles) of H13 measured around the half alignment revival of C_4H_2 in the one-color driving laser field. Error bars represent the standard deviations of nine independent measurements. The red line shows the time-dependent degrees of molecular alignment $\langle \cos^2 \theta \rangle(t)$ retrieved from the experimental data of H13.

S2 shows the time-dependent signals (solid line with circles) of the 13th harmonic (H13) measured around the half alignment revival of C_4H_2 molecule. The one-color result has been used to determine the alignment distribution of the molecules in our experiment with the method in [2]. The red line in Fig. S2 plots the retrieved time-dependent alignment parameter $\langle \cos^2 \theta \rangle(t)$. The degree of alignment in our experiment is about 0.5 ($\langle \cos^2 \theta \rangle_{max}$). It is a typical level of molecular alignment in experiment.

On the other hand, to extract the CM dynamics, multiple experimental observables are

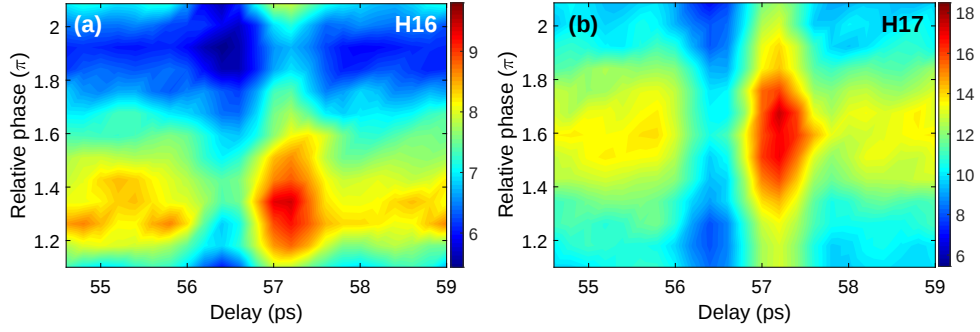


FIG. S3: HHG signals of H16 (a) and H17 (b) measured as around the half alignment revival of C_4H_2 as a function of the relative phase of the two-color driving field.

required to decompose the multichannel contributions. In our experiment, we adopt a parallel two-color driving scheme. As shown in Fig. S1, a type-I BBO crystal is installed in the arm of P_2 to produce a second harmonic (SH) field of the 800 nm fundamental laser. A calcite plate is set to compensate the group-velocity dispersion between the SH and fundamental fields. The relative phase between the SH and fundamental fields is controlled by a pair of wedges. A wire grid polarizer (WGP) is used to ensure the same polarizations of the SH and fundamental fields. The relative intensity between the SH and the fundamental fields is controlled by the combination of a dual-wave plate (DWP, a half wavelength plate at 800 nm and full wavelength plate at 400 nm) and the WGP. In our two-color experiment, the 800 nm laser intensity has been estimated from the harmonic cutoff, which is about $0.95 \times 10^{14} \text{ W/cm}^2$. The intensity of the SH field is about 2×10^{-3} of the fundamental field. In Figs. S3(a)-(b), we plot the HHG signals of both the even (H16) and odd (H17) harmonics measured around the half alignment revival of C_4H_2 in the two-color laser field. One can see that the measured HHG signals depend sensitively on the relative phase of the two-color field, and different harmonic orders present different dependencies. Considering the negligible influence of the SH field on the electron dynamics (see below), the measurements in the two-color field thus can replenish the data set required for the decomposition of the multichannel contributions.

2. Influence of the SH field on the electron dynamics

To examine the influence of the SH field in our two-color driving scheme on the induced electron dynamics in C_4H_2 molecule, we have performed three-dimensional simulations based

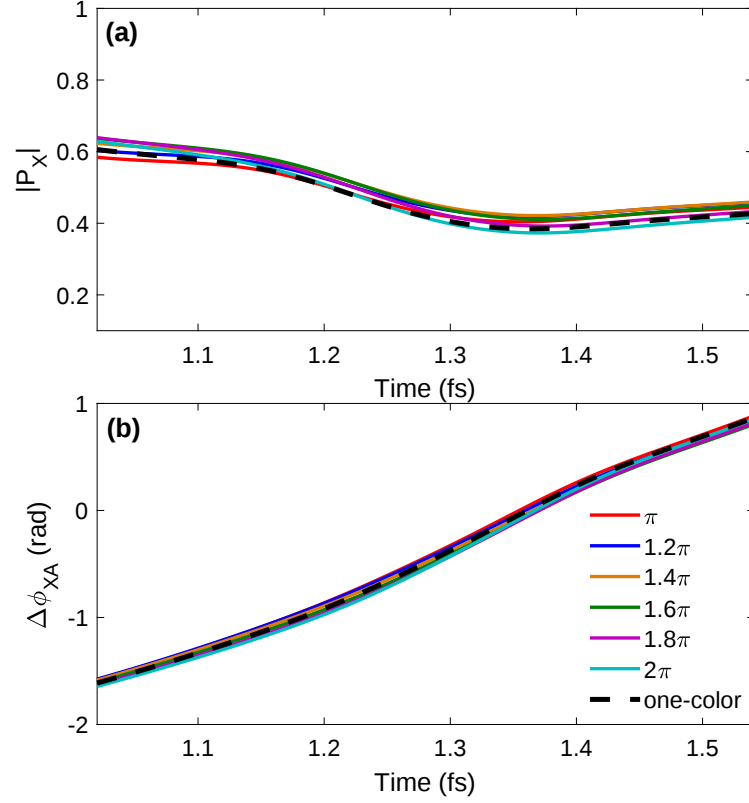


FIG. S4: (a) TDDFT calculations of the time-dependent population amplitudes of the $\tilde{X}$ state of $C_4H_2^+$ ion for different relative phases of the two-color laser fields (solid lines). The dashed line shows the result calculated with the fundamental pulse alone for comparison. (b) Same as (a), but for the relative phase between the wave functions of $\tilde{X}$ and $\tilde{A}$ states of the $C_4H_2^+$ ion.

on the time-dependent density functional theory (TDDFT). In the TDDFT framework, the molecular system is described by a series of one-particle Kohn-Sham (KS) orbitals, of which the evolution can be obtained by solving the time-dependent Kohn-Sham (TDKS) equations [3, 4]. The inclusion of laser-induced coupling between different orbitals in the TDKS equations allows us to simulate the evolution of different orbitals during the driving laser field. In our calculations, the TDKS equations are solved by using the OCTOPUS package [5] with a LDA exchange correlation functional [6] and an average-density self-interaction correction [7]. With the time-dependent TDKS orbital $\Psi_i(\mathbf{r}, t)$, the transition amplitude C_{ij} can be calculated by $C_{ij} = \langle \Psi_j(\mathbf{r}, 0) | \Psi_i(\mathbf{r}, t) \rangle$, where $\Psi_j(\mathbf{r}, 0)$ is the initial KS orbital and the subscript denotes the $\tilde{X}$ and $\tilde{A}$ states involved in the CM dynamics. Then the complex amplitude of each orbital can be obtained by $P_j = \sum_i C_{ij}(\theta) \gamma_i(\theta)$ [8, 9], where

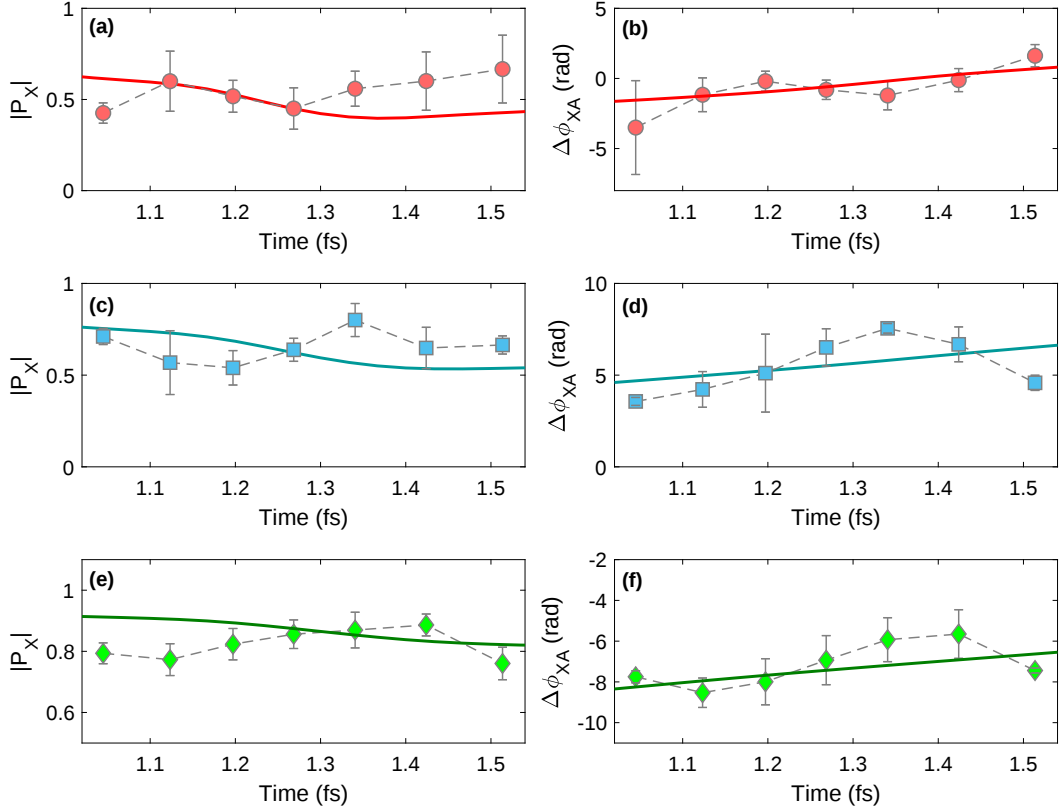


FIG. S5: (a)-(b) Retrieved population amplitude of the $\tilde{X}$ state (a) and the relative phase between the wavefunctions of $\tilde{X}$ and $\tilde{A}$ states (b) in C_4H_2 for the alignment angle of 15° . Solid lines in (a)-(b) show the corresponding TDDFT results for comparison. (c)-(d), (e)-(f) Same as (a)-(b), but for the alignment angles of 45° and 75° , respectively.

$\gamma_i(\theta)$ is the initial population of the state i , which is associated with the ionization rate $\eta_i(\theta)$ of each orbital by $|\gamma_i(\theta)|^2 = \eta_i(\theta) / \sum_i \eta_i(\theta)$. Here, the ionization rates $\eta_i(\theta)$ of different molecular orbitals are calculated with the MO-ADK theory [10–12].

In our simulations, the two-color fields are expressed as $E(t) = E_1 \cos(\omega t) + E_2 \cos(2\omega t + \varphi)$, where E_1 and E_2 are the laser intensities of the two-color fields taken from the experiment, and φ is the two-color relative phase. Note that, to simulate the sub-cycle electron dynamics, the laser envelopes of the two-color fields have been left out in the calculation. We have performed two-color simulations for the parallel alignment of the C_4H_2 molecule, since in this case the influence of the external laser field on the electron dynamics is prominent. Figure S4(a) shows the time-dependent population amplitudes ($|P_X|$) of $\tilde{X}$ state of $C_4H_2^+$ ion calculated with different relative phases of the two-color laser field (solid lines). Figure

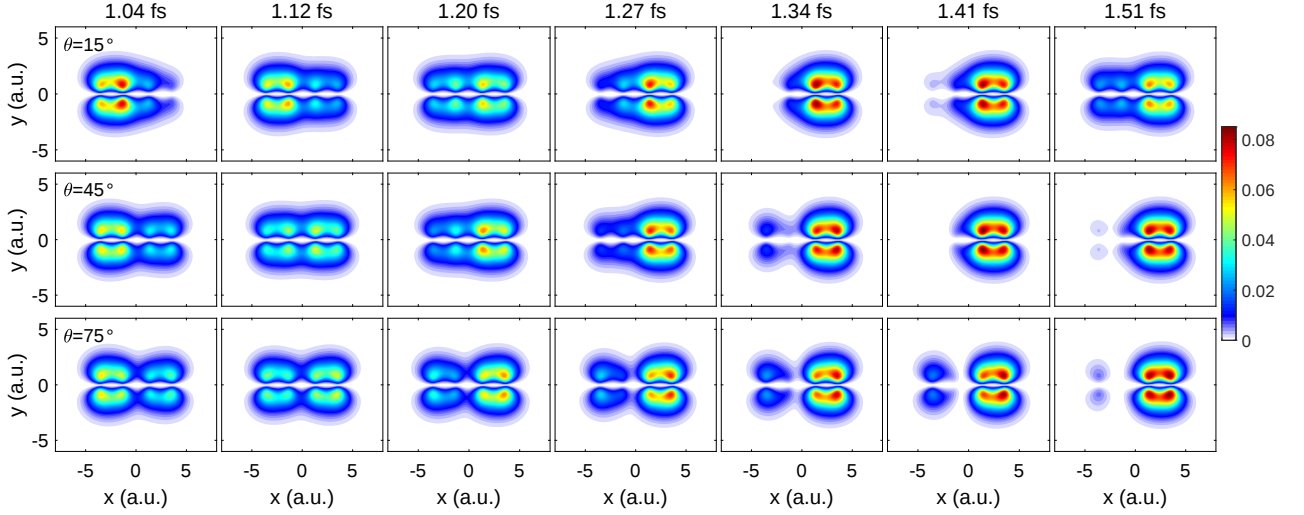


FIG. S6: Snapshots of the reconstructed hole densities for the alignment angles of 15° (top row), 45° (middle row) and 75° (bottom row), respectively.

S4(b) is the corresponding relative phases $\Delta\phi_{XA}$ between the wave functions of $\tilde{X}$ and $\tilde{A}$ states. For comparison, the results calculated with the 800 nm fundamental pulse alone are also presented as the dashed lines. It's obvious that the results (both $|P_X|$ and $\Delta\phi_{XA}$) calculated in the two-color field for different relative phases are very close to that calculated with the fundamental pulse alone, indicating the negligible influence of the weak SH field on the electron dynamics.

3. Alignment-angle-resolved CM in $C_4H_2^+$

In our reconstruction, the harmonic dipoles (both amplitude and phase) for all alignment angles of each fixed-in-space molecule are retrieved from the measured harmonic spectra. Thus the alignment-angle-dependent CM in the molecule can be fully resolved in our reconstruction. In this section, we discuss the alignment dependence of the CM dynamics in C_4H_2 molecule. Figure S5 shows the population amplitude of the $\tilde{X}$ state (left column) and the relative phase between the wavefunctions of $\tilde{X}$ and $\tilde{A}$ states (right column) retrieved from the experimental data of H11-H17 for three alignment angles of 15° [(a)-(b)], 45° [(c)-(d)] and 75° [(e)-(f)], respectively. For comparison, the TDDFT simulations of these parameters are also presented as the solid lines in each panel. One can see that the retrievals are in reasonable agreement with the simulations. With these parameters, we have constructed the hole dynamics for these three alignment angles. As shown in Fig. S6, the hole dynamics

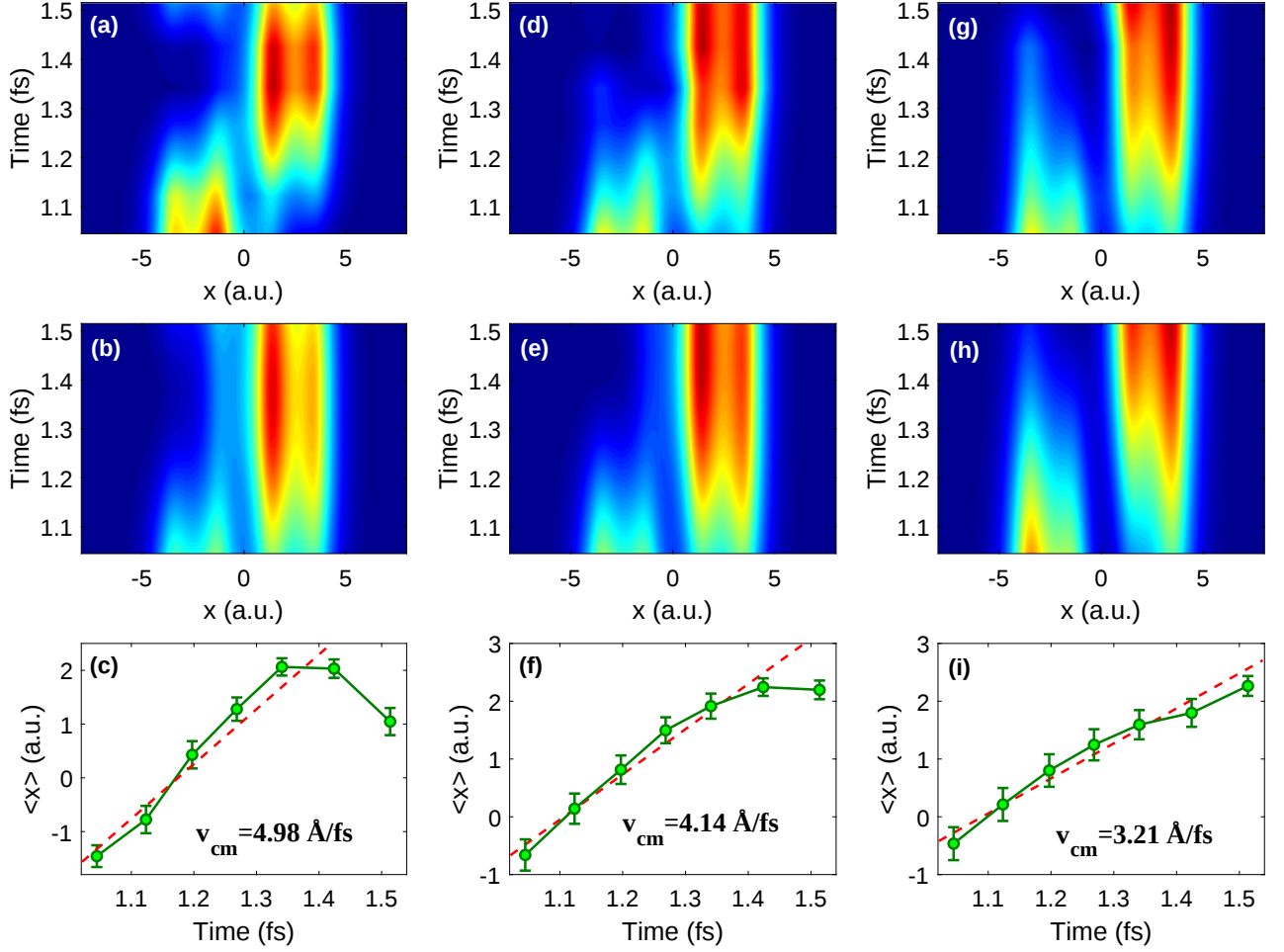


FIG. S7: (a) The reduced hole density $\rho_x(t)$ retrieved for the alignment angle of 15°. (b) Same as (a), but for the TDDFT simulations. (c) Time-dependent expected values of the x-coordinate $\langle x \rangle(t)$ (solid line with circles) calculated from the hole densities in (a). The dashed line is a linear fitting of $\langle x \rangle(t)$ to evaluate the CM speed. (d)-(f), (g)-(i) Same as (a)-(c), but for the alignment angles of 45° and 75°, respectively.

undergoes significant change as the alignment angle varies.

We have also calculated the reduced hole densities $\rho_x(t)$ for these three angles. The results are plotted in Figs. S7(a), (d), and (g), respectively. For comparison, the corresponding TDDFT simulations are also displayed in Figs. S7(b), (e), and (h). One can see good agreement between the experimental reconstructions and the theoretical simulations. Moreover, we have also extracted the time-dependent COC positions $\langle x \rangle(t)$ for these three cases [see solid line with circles in Figs. S7(c), (f), and (i)], from which the CM speeds are extracted to be 4.98 Å/fs, 4.14 Å/fs, and 3.21 Å/fs, respectively. A plot of the alignment-angle-dependent

CM speeds has been given in the main text (see Fig. 5).

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