Strong-field control and spectroscopy of attosecond electron-hole dynamics in molecules

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Molecular structures, dynamics and chemical properties are determined by shared electrons in valence shells. We show how one can selectively remove a valence electron from either II vs. Σ or bonding vs. nonbonding orbital by applying an intense infrared laser field to an ensemble of aligned molecules. In molecules, such ionization often induces multielectron dynamics on the attosecond time scale. Ionizing laser field also allows one to record and reconstruct these dynamics with attosecond temporal and sub-Ångstrom spatial resolution. Reconstruction relies on monitoring reconstructing high-frequency emission produced when the liberated electron recombines with the valence shell hole created by ionization.

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Electrons in valence molecular shells hold keys to molecular structures and properties. This article focuses on finding ways to control and record their dynamics with attosecond (1 as ≈ 10\(^{-18}\) sec) temporal resolution. Imaging structures and dynamics at different temporal and spatial scales is a major direction of modern science that encompasses physics, chemistry and biology (1). Electrons in atoms, molecules and solids move on an attosecond timescale; resolving and controlling their dynamics are goals of attosecond and strong-field science (2–6).

A natural route in manipulating valence electrons is to apply laser pulses with electric fields comparable with the electrostatic forces binding these electrons in molecules. Combination of pulse-shaping techniques and adaptive (learning) algorithms (7–16) turn intense ultrashort laser pulses into “photonic reagents” (8), allowing one to steer molecular dynamics toward a desired outcome by tailoring oscillations of the laser electric field. Strong-field techniques find applications in controlling molecular reactions (9, 14), nonadiabatic coupling of electronic and nuclear motion (15), suppression of decoherence (16, 17), etc. From the fundamental standpoint, one of intriguing challenges lies in understanding and taming the complexity of strong-field dynamics, where multiple routes to various final states are open simultaneously and multiple control mechanisms operate at the same time.

Although nuclei in molecules move on the femtosecond time scale, attosecond component of the electronic response often plays crucial role (see, e.g., ref. 18). For example, in polyatomic molecules electronic excitations in intense infrared laser fields are created via laser-induced nonadiabatic multielectron (NME) transitions (14, 19, 20). These transitions occur on the sublaser cycle time scale and determine femtosecond dynamics that follows. Although laser-induced NME transitions open multiple excitation channels (14) and lead to molecular breakup into a multitude of fragments (15, 19, 20), in practice, they can be hard to control. We show that tunnel ionization in low-frequency laser fields is an alternative way of creating a set of electronic excitations in the ion, which can be controlled by changing molecular alignment relative to laser polarization. The control mechanism uses symmetries of molecular orbitals to remove an electron from either II vs. Σ or bonding vs. nonbonding orbital. Increasing laser wavelength λ suppresses runaway nonadiabatic excitations (19) while keeping ionization channels intact. Control over the initial electronic excitation is a gateway to controlling molecular fragmentation that follows.

Because tunnel ionization can create electronic excitations, the hole left in a molecule will move on an attosecond time-scale determined by inverse energy spacing between excited electronic states, \( \tau \approx h/\Delta E \). How can one image such motion? Using attosecond probe pulses is problematic: necessarily high carrier frequency of such pulses interacts with core rather than valence electrons. The electron current also does not record hole dynamics, see below. However, when ionization occurs in a laser field, the liberated electron does not immediately leave the vicinity of the parent ion: Oscillations in the laser electric field can bring the electron back (21). We show how the hole dynamics is recorded in the spectrum of the radiation emitted when the liberated electron recombines with the hole left in the molecule.

Results

We first consider control of optical tunneling. Consider an example of a CO\(_2\) molecule interacting with intense infrared laser field. The critical factors in strong-field tunnel ionization are the ionization potential \( I_p \) and the geometry of the ionizing orbital (22, 23). Removal of an electron, which leaves the ion in an electronic state \( j \), is visualized using the Dyson orbital \( \Psi_D j = \sqrt{N} \langle j | \Psi^{(N-1)} \rangle | j \rangle \). Here, \( \Psi^{(N)} \) is the N-electron wave function of the neutral molecule and \( \Psi^{(N-1)} \) describes the ion in the state \( j \). Dyson orbitals for the ground state \( X\bar{2}^1\Pi_u (\tilde{i} = X) \) and the first two excited states \( A\bar{2}^2\Pi_u (\tilde{i} = A) \) and \( B\bar{2}^2\Pi_u (\tilde{i} = B) \) of the CO\(_2\) molecule are shown in Fig. 1A and C. Because tunnel ionization is exponentially sensitive to \( I_p \), one would expect that only ground state of the ion is excited after ionization, i.e., \( X \) is the only participating ionization channel.

However, the nodal structure of \( \Psi_{D,X} \) (Fig. 1A) suppresses ionization for molecules aligned parallel or perpendicular to the laser polarization. Indeed, opposite phases of the adjacent lobes in \( \Psi_{D,X} \) lead to the destructive interference of the ionization currents for molecular alignment angles around \( \Theta = 0^\circ \) and \( \Theta = 90^\circ \), as observed in the experiment (24). Due to the interference suppression of ionization in the \( X \)-channel, ionization channels with higher \( I_p \) (e.g., \( A, B \)) become important. For the ion left in the first excited state \( A\bar{2}^1\Pi_u \) (Fig. 1B), the same argument shows that ionization is suppressed near \( \Theta = 0^\circ \) but enhanced near \( \Theta = 90^\circ \), perpendicular to the molecular axis. In the latter case, there is no destructive interference between the adjacent lobes with the opposite phases, because only the lobe near the “down-
For the ion left in the second excited state bending" part of the ion potential will contribute into ionization. If several electronic states of the cation are excited, will the hole move, and how? Consider alignment angles near 90°, where the two ionization channels (A and X) are significant, see Fig. 1D. Note that probability of ionization for X-channel is strongly suppressed for Θ = 90°, but not equal to zero. Destructive interference occurs only for the electrons ejected along the laser field, exactly perpendicular to the molecular axis. Although such electrons dominate the ionization current from each lobe, there is a certain amount of electrons ejected in all other directions, i.e., at angles different from 90° with respect to the molecular axis. Such electrons are responsible for the ionization probability when the laser field is orthogonal to the molecular axis. The presence of these electrons is a consequence of the Heisenberg’s uncertainty principle and the confinement of the continuum wave packets when the laser field is orthogonal to the molecular axis. Although such interference occurs only for the electrons ejected along the laser field, exactly perpendicular to the molecular axis, and hence, for this choice of |p), the projection (|p|Φ_{C,A(t)}) = 0, and the hole is "static," with only Ψ_{N}^{−1} present in the superposition.

Fig. 1. Dyson orbitals corresponding to different ionization channels of CO₂. (A) X. (B) A. (C) B. Red and orange correspond to positive and negative lobes. The orbitals are shown at the level of 90% of the electron density. (D) Shown is the degree of control over strong-field ionization amplitudes, as a function of molecular alignment angle θ: green and blue curves show control over electron detachment from II vs. Σ orbital, the red curve shows control over electron detachment from bonding (channel A) vs. nonbonding (channel X) orbital. The plotted value is the ionization amplitude (square root of probability) at the peak of the electric field, which is the relevant quantity for the process of harmonic generation discussed later. The laser wavelength is λ = 1,140 nm, and the intensity I = 2.2 × 10^{14} W/cm².
Fig. 2. Qualitative picture of the hole dynamics: evolution of the coherent superposition of the Dyson orbitals corresponding to $X$ and $A$ states of the ion. The hole moves along the molecular axis with period of 1.18 fsec. Two snapshots, shown in (i) red and orange and (ii) light and dark blue are separated by half-period and correspond to the two turning points of the hole motion. The snapshots are shown at the 40% level of the electron density. The initial conditions in the figure correspond to the “minus” superposition, $\psi_{\text{Dyson}}^{(-)} = (\psi_{X}^{(t_0)} \psi_{Y}^{(t_0)} - \psi_{X}^{(t_0+\pi)} \psi_{Y}^{(t_0+\pi)})$.

determines the relative phase of the projections $(p|\Phi_{X})$ and $(p|\Phi_{A})$, and, hence, the direction of the hole motion.

Let the ionizing electric field point vertically downward in Fig. 1 $A$ and $B$, so that the electron tunnels upwards. Since the tunneling wave packets $\Phi_{X}$, $\Phi_{A}$ are confined transversely, the Heisenberg uncertainty relationship dictates that, for both wave packets, the outgoing electron can have a range of momenta with nonzero projections on the molecular axis. For the $X$ channel, the symmetry of $|\Psi_{BS}\rangle$ also dictates that (i) the tunneling wave packet $\Phi_{X}$ will have a nodal plane along the vertical direction, and (ii) the projection $(p|\Phi_{X})$ will change its sign depending on the direction of the electron escape. In the tunneling limit, for direction of electron escape pointing into the upper left quadrant of Fig. 1 $A$ and $B$, both $(p|\Phi_{X})$ and $(p|\Phi_{A})$ are positive at the moment of ionization (“plus” superposition $\psi_{\text{Dyson}}^{(+)}$, Fig. 2 light and dark blue) and the hole starts on the left side. If direction of electron escape points into the upper right quadrant, then at the moment of ionization $(p|\Phi_{X}) < 0$ is negative, but $(p|\Phi_{A}) > 0$ is positive (superposition $\psi_{\text{Dyson}}^{(-)}$, Fig. 2, red and orange) and the hole starts on the right side. Both directions of the electron escape are equally probable. Thus, equal number of holes will move right to left and vice versa, with the electron-hole entanglement and the electron momentum $p$ selected by the measurement defining the direction.

The situation changes gradually as we rotate the electric field away from $\Theta = 90^\circ$, so that tunneling along the electric field is no longer orthogonal to the molecular axis. For the $X$ channel, this changes the relative number of electrons escaping toward the upper left vs. the upper right quadrant of Figs. 1 (a). For example, for $\Theta < 90^\circ$, more electrons will escape toward the upper right quadrant, and hence more holes will start on the right side.

We now turn to attosecond spectroscopy of valence shell holes as a tool for visualizing control over strong-field ionization that can be achieved. To record hole dynamics, which reflect the population of several ionic states, one has to record the interference between different ionization channels with variable time delay after ionization. To record the interference, a measurement must bring the system to the same final state. Only then different quantum pathways (here, ionization channels) will interfere. Thus, measuring the tunneled electrons will not do—different ionization channels leave the ion in different final states and, hence, the electronic wave packets correlated to different ionization channels will not interfere.

Interference of different ionization channels is recorded in the spectrum of radiation emitted when the liberated electron recombines with the hole left in the molecule. Fig. 3. This process, known as high-harmonic generation, returns the molecule to the same ground state it has started from, ensuring interference of different electron-hole states evolving between ionization and recombination. In the language of pump-probe spectroscopy, strong-field ionization acts as a “pump,” and recombination acts as a “probe” (28, 29). Recombination occurs within a fraction of the laser cycle after ionization, Fig. 3B. The time of ionization is linked to the time of recombination (Fig. 3B), the latter is mapped onto the harmonic number (Fig. 3C). Thus, each harmonic makes a snapshot of the dynamics for a different “pump-probe” delay, providing a “frame” for the attosecond “movie.”

This idea has already been used to track the motion of protons on attosecond time scale (28), but extending the method to electrons proved problematic. Indeed, in the pump-probe spectroscopy an important ingredient is the ability to calibrate the pump-probe signal against that obtained without pump-induced excitations. Unfortunately, the HHG process does not allow one to turn the pump off while keeping the probe on. Thus, one needs a different calibration scheme. The key ingredient of the approach (28, 29) was the ability to slow protons down by replacing them with heavier deuterons, thus calibrating intensity modulation in the harmonic spectra and reconstructing the dynamics. But how to slow down the electrons? We solve this problem by using molecular alignment to control the hole. The comparison of harmonic signals for different alignment angles simplify interpretation of our results.

Formally, the harmonic emission results from recombination, which is described by the matrix element $D(t) = \langle \Psi_{n}(t)|d|\Psi_{D}^{(n)}(t)\rangle$. Emitted light is given by the Fourier transform of $D(t)$. Relative phases, accumulated by $a(t)$ in the wave packet $\Psi_{D}^{(n)}(t)$ between ionization and recombination, lead to

Fig. 3. The origin of high temporal resolution in HHG spectroscopy. (A) Physical mechanism: Intense IR laser field liberates an electron. Within a fraction of the laser cycle, the electron is returned to the parent ion by the oscillating field. Recombination is accompanied by the emission of a harmonic photon. (b) The moment of ionization $t_i$ is linked to the moment of recombination $t_r$. Solid blue curve shows one oscillation of the laser field $E_{\text{Laser}}$, straight lines connect moments of ionization $t_i$ and recombination $t_r$. (C) The time delay between ionization and recombination $\Delta t = t_r - t_i$ is mapped onto harmonic number: $N_{\text{HHG}} = E_p(\Delta t) + I_p$. Here, $E_p$ is the energy of the returning electron.
constructive or destructive interference of different ionization channels in emission, suppressing or enhancing harmonics. This is the amplitude modulation we are looking for. Changing molecular alignment, we control the relative amplitudes of the channels and, hence, the modulation depth.

In addition to the phase accumulated in the ion, the relative phase between the channels includes contributions from the oscillatory continuum motion in the laser field and the scattering phase encoded in the recombination matrix elements. Analysis is simple for high-energy harmonic photons $N_{\text{tho}} \gg E_A - E_X$ (see supporting information (SI)). Then the relative phase accumulated in the ion is $\phi \approx (E_A - E_X) \tau$, where $\tau$ is the channel-average time delay between ionization and recombination. The phases of the oscillatory continuum motion differ much less, see SI. The phases of the recombination matrix elements, when different for the two channels, affect their interference.

Now consider the amplitude structures near $\Theta = 0^\circ$, see Fig. 4A and 5A. Here, ionization creates a wave packet of $\hat{X}$ and $\hat{B}$ states, which corresponds to a breathing motion perpendicular to the molecular axis, see Fig. 5C. The example at $\Theta = 0^\circ$ illustrates additional difficulties in the reconstruction. The contribution of the channel $\hat{X}$ is modulated by the deep structural minimum around $H_{55}-H_{59}$, associated with the geometry of $\Psi_{D.X}$. As a result, the relative contributions of the two channels into the total signal vary significantly, obscuring their interference. Furthermore, the way the period of the hole motion is recorded in the harmonic spectrum depends on the relative phase of recombination between the two channels. Accurate recording of this period in the harmonic spectrum requires that this phase does not strongly depend on energy. This requirement is violated in the vicinity of the structural minimum in the channel $\hat{X}$, where the phase of recombination changes by about $\pi$. Thus, the presence of the structural minimum will affect not only our ability to accurately reconstruct the period of the hole motion, but also our ability to accurately record it in the harmonic spectra.

**Discussion**

Consider first the structures around $\Theta = 90^\circ$, marked with arrows. Fig. 4B shows amplitudes (square roots of intensities) of the total signal and of the channels $\hat{A}$ and $\hat{X}$, for $\Theta = 90^\circ$. The channels give comparable contributions for a broad range of harmonics, which record channel interference. Constructive interference occurs around $H_{39}$, whereas destructive interference occurs around $H_{71}$. Another destructive minimum becomes visible when the signal at $\Theta = 90^\circ$ is normalized by the signal at smaller angles (here, $\Theta = 70^\circ$), Fig. 4C. As $\Theta$ changes from $\Theta = 90^\circ$ to $\Theta = 70^-0^\circ$, the channel $\hat{X}$ begins to dominate the spectrum. Thus, such normalization allows one to calibrate the “pump-probe” signal against the “time-independent” background. As $\Theta$ changes from $\Theta = 90^\circ$ to $\Theta = 60^\circ$, the minima do not move to different harmonic order, but gradually disappear, reflecting the decreasing contribution of the channel $\hat{A}$. Time delays between ionization and recombination for different harmonics are given in Fig. 4C, bottom axis. The minima appear at $H_{21}-23$ and $H_{71}$, which is normalized by the field-free period of 1.18 fs. The error in the time-energy mapping is larger for low harmonic numbers such as $H_{21}-23$. The time delay between the frames $H_{71}$ and $H_{39}$ gives half a period of the hole motion $0.63 \pm 0.08$ fs, yielding the period $1.26 \pm 0.11$ fs (see SI for the discussion of the harmonic order-time delay mapping and error bars).

Now consider the amplitude structures near $\Theta = 0^\circ$, see Fig. 4A and 5A. Here, ionization creates a wave packet of $\hat{X}$ and $\hat{B}$ states, which corresponds to a breathing motion perpendicular to the molecular axis, see Fig. 5C. The example at $\Theta = 0^\circ$ illustrates additional difficulties in the reconstruction. The contribution of the channel $\hat{X}$ is modulated by the deep structural minimum around $H_{55}-H_{59}$, associated with the geometry of $\Psi_{D.X}$. As a result, the relative contributions of the two channels into the total signal vary significantly, obscuring their interference. Furthermore, the way the period of the hole motion is recorded in the harmonic spectrum depends on the relative phase of recombination between the two channels. Accurate recording of this period in the harmonic spectrum requires that this phase does not strongly depend on energy. This requirement is violated in the vicinity of the structural minimum in the channel $\hat{X}$, where the phase of recombination changes by about $\pi$. Thus, the presence of the structural minimum will affect not only our ability to accurately reconstruct the period of the hole motion, but also our ability to accurately record it in the harmonic spectra.
To identify channel interference over a strongly modulated background, we again calibrate the results against $\Theta = 10^\circ,20^\circ$, where geometry-induced modulation of the channel $\tilde{X}$ is still present, but the contribution of the channel $\tilde{B}$ is less and the hole is almost static. Therefore, by normalizing to $\Theta = 10^\circ,20^\circ$ we accentuate the effect of the hole motion while decreasing the effect of structural modulations. The interference minimum appears at $H43$ (see Fig. 5B). Searching for the second minimum, one has to take into account the sign flip of the recombination matrix element for channel $\tilde{X}$, turning second position of the destructive interference around $H77$ into constructive (see Fig. 5B). Note, that it also turns constructive interference around $H61$ into destructive. The delay between $H77$ and $H43$ should correspond to the period of hole motion and is $0.76 \pm 0.1$ fsec. However, the relative phase between the channels $\tilde{X}$ and $\tilde{B}$ (Fig. 5C) indicates that the first destructive minimum should appear at $H39$. The delay between $H77$ and $H39$ is $0.84 \pm 0.1$ fsec, close to the field-free period of $0.96$ fsec. The appearance of the amplitude minimum at $H43$–$H45$ instead of $H39$ is due to the fast structural minimum of one of the participating channels, because there, the phase of recombination for the channel is changing rapidly. For example, we find that at 800 nm the destructive interference between the channels $\tilde{X}$ and $\tilde{B}$ occurs not at $\tau^* = 1.65$ fsec but at $\tau^* = 1.2$ fsec.

Reconstructed periods are close to those of the field-free motion for several reasons. First, in both cases we monitor hole dynamics with the laser field orthogonal to the motion. Second, laser-induced dynamics between the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states of the $\text{CO}_2^+$ ion between ionization and recombination, which is included in our calculation, is weak in the IR range. Finally, the laser-induced polarization, e.g., relative Stark shifts, which is also included in our calculation, is also small. The deviation from the field-free periods for the hole motion perpendicular to molecular axis (Fig. 5D) is due to the structural minimum in the channel $\tilde{X}$ as discussed above.

We have demonstrated the possibility to control the removal of bonding (channel $A$) vs non-bonding (channel $\tilde{X}$) electron for the ionization from $\Pi$ vs $\Sigma$ states ($A$ or $\tilde{B}$ channels) on $\text{CO}_2$ molecule. The control parameter is the molecular alignment angle $\Theta$. We used HHG spectroscopy to visualize the control that can be achieved. The dynamics of hole recorded in harmonic spectra indicates and characterizes population of several ionic states after ionization.

The potential of HHG spectroscopy is not limited to the example considered here. Analogous technique can be applied to study nonadiabatic multielectron dynamics (19) excited by the laser field and determining fragmentation pathways for polyatomic molecules subjected to strong laser field. Attosecond dynamics in the ion can also be induced by spin-orbit coupling (32). Strong-field ionization of a state with well-defined orbital angular momentum creates coherent superposition of ionic ground states with different total momenta. Mapping the evolution of this superposition into harmonic spectrum resolves spin-orbit coupling in time.
Another example is hole dynamics induced by one-photon ionization with a single attosecond XUV pulse, phase-locked to the oscillation of the IR laser field. The liberated electron, oscillating in the laser field, can still recombine with the hole, emitting harmonics. As long as the duration of the UV pulse is less than quarter-cycle of the IR, time resolution is determined by the principle shown in Fig. 3. Controlling polarization of the ionizing XUV pulse relative to the molecular axis and to the polarization of the IR field offers the possibility of controlling hole excitation. Delaying ionizing pulse relative to the phase of the oscillations of the IR field provides additional control knob in decoding attosecond-resolved signal. Such arrangement should provide a versatile setup for attosecond spectroscopy of multielectron dynamics.

Methods

Harmonic generation results from time-dependent polarization $\mathbf{D}(t)$ induced in a molecule by the incident laser pulse. Generalizing (33), we write $\mathbf{D}(t)$ as:

$$
\mathbf{D}(t, \Theta) \propto \sum_{i,j} a_{\text{ion},i}(t, \Theta) a_{\text{prop},j}(t, \Theta) \times
$$

$$
\langle \Phi_{N}^{i}(t, \Theta) | \hat{A} \Phi_{N}^{j}(t, \Theta) \rangle
$$

This general expression provides a convenient framework, which allows one to go beyond such approximations as the single-active electron approximation and the strong-field approximation. $N$-electron wave function $\Phi_{N}^{i}$ describes evolution of the neutral molecule during the laser pulse, including depletion by ionization. $\Phi_{N}^{j}$ describes multielectron dynamics of the ion starting in state $j$ at the moment of ionization $t_{j}$, until recombination at $t$. Continuum electron is described by the scattering state $\Phi_{C}$, correlated to the state of the ion $\Phi_{N}^{j}$ and characterized by the (asymptotic) kinetic momentum $k(t)$ acquired from the laser field (see S1). $\hat{A}$ is antisymmetrization operator. Angle $\Theta$ characterizes molecular alignment. We also include auto-correlation function associated with nuclear motion for each channel (29, 36) (see S1). Note, that Eq. 1 obtains by the evaluation of the integral over ionization times using the saddle point method, and thus includes the sum over all saddle points $t$. The applicability of the method relies on the large action accumulated by the continuum electron in the strong laser field (34). In our calculations we include only short trajectories to model experimental conditions, thus a single $t$ corresponds to each $t$.

The amplitude of each channel includes ion-state-specific subcycle ionization amplitude $a_{\text{ion},i}(t)$ at the moment $t$ and the propagation amplitude $a_{\text{prop},j}(t)$ between $t$ and $t_{j}$. Different ionic states can be populated by ionization or excited by non-adiabatic transitions (35) in the ion between ionization and recombination, and we include both mechanisms. The bound states, Stark shifts, dipole couplings between different ionic states are calculated using quantum chemistry methods (see S1). Harmonics are given by the Fourier transform of Eq 1.

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Bound Electrons. We use complete active space self-consistent field method to calculate 22-electron wave function of CO$_2$ and 21-electron wave functions of the ionic states $\tilde{X}, \tilde{A}, \tilde{B}$ of CO$_2^+$. For the three relevant electronic states of the ion, we correlate 15 electrons in 10 active orbitals, using correlation-consistent basis set of triple-$\zeta$ quality in the valence region (cc-pVTZ). Polarization of the electronic states by the external laser field has been calculated in the quasistatic approximation, both for the neutral and for the ion. The difference between the Stark shifts of the neutral and ionic ground states remains very small even at high intensities, reaching only $\approx 0.5$ eV at $I \approx 10^{14}$ W/cm$^2$. Distortions of the reduced single-electron density by the static external field at these intensities also remain small. The Stark shifts of the neutral ground states and the ionic states are included in the ionization potentials for calculating ionization amplitudes for different ionization channels. We also calculate the transition dipole moments between the essential ionic states and use them to describe laser-induced dynamics in the ion between ionization and recombination within a restricted basis of $\tilde{X}, \tilde{A}, \tilde{B}$ states. These states can be populated by ionization or excited by laser-induced nonadiabatic transitions in the ion between ionization and recombination. We treat both mechanisms, but the latter is negligible for CO$_2^+$ at $\lambda = 1,140$ nm.

Continuum Electron. Continuum dynamics includes three components: ionization, propagation of the continuum electron between ionization and recombination, and recombination.

Ionization is calculated using the method of refs. 1–5 to include the geometry of the Dyson orbital. The Coulomb-corrected subcycle ionization rates are taken from ref. 6. To account for the multicenter geometry of the Dyson orbital, it is written as a linear combination of spherical atomic orbitals. This representation allows us to factorize the ionization amplitude, approximating it as a product of the “atomic” ionization amplitude $a_{\text{ion}}(R, \Theta)$ from a single atomic orbital and an angular-dependent term $R(\Theta)$, determined by the interference of the atomic orbitals and given by the Fourier transform of the Dyson orbital into the momentum space.

The “atomic” ionization amplitude takes into account the relative Stark shift between the ground state of the neutral and the final ionic state, calculated in the quasistatic approximation (see subsection on bound electrons above). To calculate the suboptimal cycle “atomic” ionization amplitude, we use the Yudin–Ivanov formula (6), including the Coulomb corrections as described in ref. 6.

Our analytical approximation to $R(\Theta)$ uses the method described in ref. 5. The Fourier transform is first squared and then integrated with the tunneling-induced momentum filter for the outgoing electron, yielding $R^2(\Theta)$. The momentum filter is Gaussian in the direction perpendicular to laser polarization, with the width determined by the Keldysh tunneling time $\tau_T = \sqrt{2\hat{p}E/T}$, where $E$ is the electric field amplitude for the given cycle of the multicycle laser pulse.

Following standard approach (7), the propagation amplitude is approximated as

$$a_{\text{prop}}(t, t_i, \Theta) \approx (t - t_i - i\tau_T(t_i))^{{-3/2}}v^2F_+(\Theta) \quad [S1]$$

Here, $\tau_T(t_i)$ is the Keldysh-type quasistatic subcycle tunneling time $\tau_T(t_i) = \sqrt{2T_p} |E(t_i)|$, where $E(t)$ is the electric field at the moment of ionization. To take into account characteristic transverse size $\Delta r_{\perp}$ of the ionizing state, we use the approximation $1/\Delta r_{\perp} \approx \sqrt{\tau_T + \Delta \tau}$ for the transverse spreading velocity $v_{\perp}$. The contribution to the spreading velocity due to characteristic size of the Dyson orbital has been determined directly from the Fourier transform of the orbital. Correction to the connection between $t_i$ and $t_f$ due to the attractive long-range Coulomb tail of the ionic potential is included as described in (8). The angle-dependent factor $F_+(\Theta)$ includes the contribution of the nodal planes of the ionizing orbital to the transverse shape of the continuum wave packet.

Strong-field eikonal Volkov approximation (8) in combination with additional adiabatic approximation (9) (SFEVA+AAA) takes care of continuum dynamics during recombination, including channel-specific approximations on the parent ion during the ionization. To find the scattering state $\phi_{\text{scat}}(t_i, k(t), \Theta)$, we need to know the electron-ion interaction potential. We approximate it as $U_{\text{Hartree}}(t_f, t) + U_{\text{nuclear}}$, including the Coulomb potential of the nuclei (C–O distance equal to 1.1621 Å) and the Hartree potential of the bound electrons for the ionic state corresponding to the channel $j$. The Hartree potential was calculated by the numerical solution of the Poisson equations on a uniformly spaced ($d = 0.116$ Å) numerical grid in a 69.7-Å cubic box. Calculation of the asymptotic momenta $k(t)$, which characterize the scattering states is discussed in the next section.

Asymptotic Momentum $k(t)$. Scattering state is characterized by the asymptotic momentum $k(t)$. We find it by setting the asymptotic kinetic energy of the returning electron $E_{\text{kin}}(t_f) = k(t)^2/2$ to that acquired by the electron from the laser field. It includes important correction to the standard term $[a(t_i) - A(t_i)]^2/2$: $E_{\text{kin}}(t) = [A(t) - A(t_i)]^2/2 + \Delta E(t)$ and, hence, $k(t) = A(t) - A(t_i) + \Delta k(t)$. Here $A(t)$ is the vector-potential of the laser field, with electric field $E(t) = -\alpha A(t)/\partial t$. The correction $\Delta E$ comes from the fact that after ionization the characteristic electron trajectory starts at a distance $z(t_i)$ away from the origin. For arbitrary phase of birth, this distance is given in (8). The liberated electron has to cover this extra distance on the way back before recombination. Additional energy acquired by the electron from the laser field over this distance increases the electron recombination energy for short trajectories. Near the cutoff, this extra energy equals 0.32 $I_p$ (10). For ionization potentials of $I_p \approx 15–19$ eV the corresponding correction of 5–6 eV $\approx 3–4$ $\omega_0$ is very significant.

Relative Phase of Different Channels. Dynamical interference minima in harmonic amplitudes occur when channels contributing to the harmonic signal interfere destructively.

The phase of each channel (labeled with index $j$) has three main contributions: the phase accumulated in the ion, the Volkov phase due to the oscillations of the continuum electron and the phase of the recombination dipole matrix element due to the scattering of the continuum electron on the parent ion. In low-frequency fields with large average oscillation energy $U_p \gg \omega_0$ for each harmonic photon with energy $\omega_0$ there is a well-defined delay time $\tau_j = \tau_j(\omega_0) = t_j(\omega_0) - t_j(N_0)$ between ionization and recombination. In this limit, the harmonic phase for a given channel can be written as a function of the recombination time (which is different for different channels):

$$\Phi_j(\omega_0) = \phi_{\text{scat}}[t_j(\omega_0)] + I_{jp} \times \tau_j(\omega_0) + \Phi_{\text{rec}}j - \omega_0 \times t_j(\omega_0) \quad [S3]$$

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Here $I_p$ is the ionization potential for the channel $j$, $\phi_c(t_1(N_0))$ is the continuum (Volkov) phase due to electron oscillations between ionization and recombination, $\phi_{rec}$ is the phase of the recombination dipole matrix element, and $N_0 \times t_1(N_0)$ comes from the Fourier transform. The key property important for our analysis is that the phase is stationary,

$$\frac{\partial}{\partial t} \Phi_j(t_1(N_0)) = 0 \quad [S4]$$

Let there be two channels, $j = 1, 2$ and let us express the phase of the channel $j = 2$ via the phase of the channel $j = 1$. We have:

$$\Phi_2(t_2(N_0)) = \Phi_1(t_1(N_0)) + \Delta t_1 \times \tau_2(N_0) + \phi_{rec} \quad [S5]$$

Here, we added and subtracted $I_p \times \tau_2(N_0)$ and $\phi_{rec}$ and denoted $\Delta t_1 = I_p - I_p$ and $\Delta \phi_{rec} = \phi_{rec, 2} - \phi_{rec, 1}$. This identical transformation allows us to write the phase of the channel $j = 2$ as

$$\Phi_2(t_2(N_0)) = \Phi_1(t_1(N_0)) + \Delta \phi_{rec} \quad [S6]$$

i.e., as the phase of the channel $j = 1$ calculated at a slightly different recombination time, $t = t_1(N_0)$, plus the phase difference due to dynamics in the ion $\Delta \phi_{rec}$ and the difference in the recombination phase. Now, using the fact that the phase is stationary and the first derivative with respect to $t$ is zero, we use the Taylor expansion of $\Phi_1(t_1(N_0))$ to write

$$\Phi_1(t_1(N_0)) = \Phi_1(t_1(N_0)) + \frac{\partial}{\partial t} \Phi_1(t_1(N_0)) + O(\Delta t^2) \quad [S7]$$

Here, $\Delta t = t_2(N_0) - t_1(N_0)$. Thus, we obtain the final expression

$$\Phi_2(t_2(N_0)) = \Phi_1(t_1(N_0)) + \Delta \phi_{rec} + O(\Delta t^2) \quad [S8]$$

where $\phi(N_0)$ is the channel-average time delay. As long as $N_0 \gg \Delta \phi_{rec}$, the difference $\Delta t$ between the two channels is small and the quadratic terms $O(\Delta t^2)$ are negligible.

Compared to $\Delta \phi_{rec}(N_0)$, relative phases of the recombination matrix elements for the two channels change slowly as a function of harmonic number, except for the vicinity of the structural minimum for a specific channel, where the corresponding recombination matrix element switches the sign.

**Selection of Quantum Trajectories.** In single-molecule response, there are several so-called “quantum” trajectories of the liberated electron that return to the parent ion with the same electron energy but at different times $t$. These trajectories are grouped into “short” and “long,” depending on whether they return to the parent ion before or after the highest-energy trajectory with the energy $= 3.2U_0$ (here, $U_0$ is the average oscillation energy of the free electron in the laser field) (11). However, in a molecular gas propagation of harmonic radiation associated with short and long trajectories is different, in terms of both the phase-matching and the divergence. In typical experiments on high harmonic generation, the geometry of the experimental setup suppresses the so-called “long” trajectories and favors the short ones. To account for this experimental aspect, we (i) first calculated $D(t)$ for each ionization burst (i.e., each half-cycle) and then (ii) multiplied it with a temporal Gaussian filter. The filter smoothly suppresses the signal after the most energetic $3U_0$ trajectory, for each ionization burst.

**Averaging Over Alignment Distribution.** In experiments, molecules are prealigned with an aligning pulse. When the aligning and the harmonic-generating laser pulses are polarized parallel to each other, the typical degree of alignment for the molecular ensemble is $\pm 30^\circ$ (12). This degree of alignment is well-reproduced by $\cos^\Theta$ or $\sin^\Theta$ distributions (the former having characteristic alignment angle of $\pm 32^\circ$ and the latter $\pm 28^\circ$). In our calculations, angle-averaging of the emitted light (i.e., the Fourier transform of $D(t)$) was performed with $\cos^\Theta$ distribution.

**Accuracy of Energy-Time Mapping.** For a specific channel, say channel $X$ with given ionization potential $I_X$, the harmonic number uniquely maps into time delay $\tau_X$ between ionization and recombination. Recording and reconstructing the hole dynamics implies measurement of harmonic generation for different channels. Since these channels have different ionization potentials, for different channels one would obtain different time delays for a given harmonic number. Thus, difference in ionization potentials introduces error in the definition of the time delay. The error depends on harmonic number, being relatively small for high harmonic orders $N_0 - I_p \gg \Delta \phi_{rec}$ and becoming significant for lower harmonic numbers $N_0 - I_p \sim \Delta \phi_{rec}$.

There is an additional source of error related to the fact that harmonic spectrum records interference between the channels only at discrete time delays. Therefore, one can only find the position of the minimum or maximum with the accuracy no better than the time delay between the adjacent harmonics.

These two sources of the error are independent and the total error is estimated as the square root of the sum of the squares of the individual errors.

**Effect of Nuclear Motion.** To include the effect of nuclear motion we multiply time-dependent dipole moment (see Eq. 1 of the main text) by autocorrelation function $\xi(t) = (\Psi_A(t)\Psi_A(t))$ (13). Here, $\Psi_A(t)$ is vibrational wave packet evolving on the potential energy surface of the neutral and $\Psi_A(t)$ evolves on cationic surface. Calculations use the method developed in ref. 14 and show (see Fig. 1) that nuclear motion does not affect the relative weights of channels $X$ and $\bar{B}$ in harmonic spectra and therefore do not affect their interference. In contrast, the nuclear motion much stronger affects the channel $A$, especially for the long wavelengths driving field. As the result nuclear dynamics changes the relative contributions of channels $X$ and $\bar{A}$ and slightly suppresses their interference in the cutoff region.
Fig. S1. Effect of nuclear motion on the relative contribution of different channels. Square modulus of autocorrelation function $|\langle \Psi_n(\tau) | \Psi_c \rangle|^2$. Autocorrelation function multiplies the time-dependent dipole for channels $\tilde{X}$ (red), $\tilde{A}$ (green), $\tilde{B}$ (blue).