Electronic coherences in nonadiabatic molecular photophysics revealed by time-resolved photoelectron spectroscopy

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Time-resolved photoelectron spectroscopy (TRPES) signals that monitor the relaxation of the RNA base uracil upon optical excitation are simulated. Distinguishable signatures of coherence dynamics at conical intersections are identified, with temporal and spectral resolutions determined by the duration of the ionizing probe pulse. The frequency resolution of the technique, either directly provided by the signal or retrieved at the data-processing stage, can magnify the contribution from molecular coherences, enabling the extraction of most valuable information about the nonadiabatic molecular dynamics. The predicted coherence signatures in TRPES could be experimentally observed with existing ultrashort pulses from high-order harmonic generation or free-electron lasers.

Significance

Time-resolved photoelectron spectroscopy (TRPES) is a promising technique for the study of ultrafast molecular processes, such as the nonadiabatic dynamics taking place at conical intersections. Directly accessing the evolution of the coherences generated at the conical intersection should provide most valuable dynamical information. However, the signals are dominated by background contributions due to state populations, and most theoretical treatments completely neglect the role of the coherences. Here we show that distinguishable signatures of molecular coherences appear in TRPES. These can be recorded using currently available ultrashort pulses and unambiguously extracted at the postprocessing stage. The technique thus provides direct access to nonadiabatic coherence dynamics.
basis states surface. An ultrashort pulse dependent nuclear wave packet on the I
shown in
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nonadiabatic dynamics are probed by an ionizing pulse centered
initially excited by a pump centered at
the loop diagram shown in Fig. 1. A neutral molecule is separate it from the population background.

Loop diagram of the photoelectron signal. The gray area represents

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The time-resolved photoelectron signal is represented by

The time-resolved photoelectron signal is represented by the loop diagram shown in Fig. 1. A neutral molecule is initially excited by a pump centered at \( t = 0 \), and its subsequent nonadiabatic dynamics are probed by an ionizing pulse centered at a variable time \( T \). The evolution of the molecule prior to the ionizing pulse is described by the time-dependent wave function \(|\Psi(t)\rangle = \sum |\chi_i(t)\rangle |\psi_i\rangle\), expanded in the adiabatic basis states \(|\psi_i\rangle\) of the neutral molecule. \(|\chi_i(t)\rangle\) is the time-dependent nuclear wave packet on the Ith potential energy surface. An ultrashort pulse \( E(t-T) = e E(t-T) = e E(t-T) e^{-i\omega_X(T-T)}\), of carrier frequency \( \omega_X\), polarization vector \( e\), and envelope \( \varepsilon(t)\), ionizes the molecule, leading to the emission of a photoelectron. We denote with \(|\varphi_\alpha\rangle\) the \( \alpha \)th adiabatic electronic state in the molecular ion, whereas \( k_\alpha \) labels a continuum state of the emitted photoelectron at the detected energy \( \epsilon \). The TRPES signal is obtained by energy dispersing the emitted photoelectrons as a function of the pulse arrival time \( T \). The orientationally averaged signal
\( S(\epsilon, T) = S_{pop}(\epsilon, T) + S_{coh}(\epsilon, T) \)[1] can then be partitioned into the sum of a population contribution \((I = I'); \text{Eq. 15}\) and a coherence term \((I \neq I'); \text{Eq. 16}\), as shown in Materials and Methods. The key molecular parameters required for computing the signal are the neutral \( \omega_i(q)\) and ionic \( \omega_\alpha(q)\) potential energy surfaces and the Dyson orbitals (34)
\[ \phi_{D,\alpha i}(q, r) = \sqrt{N} \int d^3r_2 \cdots \int d^3r_N \varphi^*_\alpha(q, r_2, \ldots, r_N) \psi_i(q, r, \ldots, r_N), \] [2]

between the \( Ith \) and \( \alpha \)th states, where \( q = (q_1, \ldots, q_M)\) is the vector of the \( M \) nuclear coordinates considered in the model.

For comparison, we note that the time-resolved photoelectron signal is most commonly simulated using a semiclassical expression \( S_{coh}(\epsilon, T) \) based on Fermi’s golden rule (31–33),
\[ S_{coh}(\epsilon, T) = \int d\omega |\tilde{\varepsilon}(\omega - \omega_X)|^2 S_{coh,0}(\epsilon, T, \omega), \] [3]

where \( \tilde{\varepsilon}(\omega) \) is the Fourier transform of the pulse envelope \( \varepsilon(t) \) and
\[ S_{coh,0}(\epsilon, T, \omega) = \sum_{I, k_\alpha} \langle V_{I, k_\alpha} | \Psi_{I, \alpha}(q(T)) \rangle^2 \eta_i(q(T)) \times \delta(\epsilon - \omega + \omega_\alpha(q(T)) - \omega(q(T))) \] [4]
is a reference signal for a fixed probe frequency \( \omega \), expanded on the adiabatic basis. The nuclear dynamics \( q(T) \) are simulated semiclassically, and \( \langle \cdots \rangle \) denotes an average over the nuclear coordinates weighted by the populations \( \eta_i(q(T)) \). As is apparent from Eqs. 3 and 4, the semiclassical approach completely neglects contributions due to vibronic coherences. In the following, we show that these coherence terms lead to observable signatures in the TRPES signal.

We have calculated the photoelectron signal given by Eqs. 1, 15, and 16 to probe the photorelaxation of the RNA nucleobase uracil passing through a CoIn. Uracil has drawn significant attention, both theory and experiment, because of its biological relevance, convenient size, and handleability. Various methods have been developed to calculate the photoexcited dynamics of coupled electronic and nuclear degrees of freedom at a CoIn. Traditional semiclassical surface-hopping approaches, where the nuclei are treated completely classically, miss the coherence emerging at the CoIn and therefore their signatures in the TRPES signal. More advanced semiclassical methods like ab initio multiple spawning (35) or cloning (36, 37) can capture these coherences and thus the complete TRPES signal. Another possibility is to aim for a more quantum description of the nuclear dynamics, e.g., through the multiconfigurational time-dependent Hartree method (38). Here we performed exact nuclear wave packet dynamics simulations in uracil, by using the effective Hamiltonian introduced in ref. 39 to include a completely quantum description of the nuclear degrees of freedom in the solution of the time-dependent Schrödinger equation. This model includes three adiabatic electronic states, and the dynamics are restricted to two nuclear coordinates \( q_1 \) and \( q_2 \), as shown in Fig. 2A: \( q_1 \) represents the motion from the Franck-Condon to the CoIn, whereas \( q_2 \) describes the motion from the Franck-Condon to a local minimum on the \( S_2 \) surface.

In Fig. 2B, we display the potential energy surfaces of the ground \( S_0 \) and the first two excited states \( S_1 \) and \( S_2 \) in neutral uracil, calculated at the CASSCF(12/8)/6-311G* level. There is a CoIn seam between \( S_1 \) and \( S_2 \) opening a radiationless relaxation pathway, as indicated by the black lines on the right bottom part of the panels in Fig. 2B. The ionization energies and Dyson orbitals were calculated adopting the approach described in ref. 32. Fig. 2C shows the ground \( S_0 \) and the first two excited-state surfaces \( S_1 \) and \( S_2 \) of cationic uracil (40). Their ionization energies from the minimum of the ground \( S_0 \) surface are centered between 8 and 10 eV, and the ionization energies from the neutral-molecule excited states \( S_1 \) and \( S_2 \) vary between 2 and 7 eV. These energies will appear in the photoelectron signal. Fig. 2D shows the spatial profile of the Dyson orbitals \( \phi_{D,\alpha i}(r) \) (Eq. 2) for the three neutral and ionic molecule states considered in our model and for a representative nuclear configuration, i.e., at the minimum of the \( S_2 \) surface at \( q_1 = -0.2 \) Å and \( q_2 = 0.5 \) Å. These orbitals exhibit the typical shape of valence molecular orbitals and correspond to the region in the molecule from which...
the electron is ejected upon ionization. They are mostly of \( \pi \) and \( \pi^* \) type, distributed across the entire molecular ring, with two oxygen lone pairs in the \( D_3S_0 \) and \( D_1S_2 \) transition.

The time-dependent wave function \( |\psi(\tau)| \) representing the evolution of the neutral molecule prior to the ionizing probe pulse, is calculated for a 34-fs UV pump pulse centered at \( t = 0 \) and matching the \( S_0 \rightarrow S_2 \) transition energy, which transfers populations from \( S_0 \) into \( S_2 \). The associated populations and the \( S_2/S_1 \) coherence dynamics are shown in Fig. 3A and B, respectively. After the pump excitation, the system freely evolves on the \( S_2 \) surface, until the wave packet reaches the \( \text{CoIn} \), and the nonadiabatic passage takes place, starting at approximately \( t = 100 \text{ fs} \). This is reflected in the evolution of the populations and coherences: at the \( \text{CoIn} \) passage, some population is transferred from the \( S_2 \) into the \( S_1 \) state, thereby creating a vibronic coherence between these two states.

We simulate TRPES to probe the evolution of populations and coherences along this photophysical relaxation path in uracil. We assume a Gaussian XUV ionizing pulse centered at \( \omega_{X} = 20 \text{ eV} \) and of envelope \( \mathcal{E}(t) = e^{-t^2/(2\tau^2)} \). Fig. 4A presents the total photoelectron spectrum \( S(\epsilon, T) \) for a probe pulse of duration \( \tau = 1 \text{ fs} \). The signal is dominated by populations (Eq. 15), as is apparent in Fig. 4B, which displays the weaker coherence contribution \( S_{\text{coh}}(\epsilon, T) \) due to \( I \neq I' \) (Eq. 16). The narrowband pulse used in Fig. 4 provides the frequency resolution needed to observe spectral changes due to the evolution of the molecular wave packet on the potential energy surface (41). The photoelectron energy peak reflects the local transition energy between the cationic and neutral states since \( \epsilon \approx \omega_{X} - (\omega_2 - \omega_1) \) (see also Eqs. 3 and 4). At negative time delays \( T < 0 \), when uracil is probed before the interaction with the pump, the signal is peaked at energies below 12 eV since the molecular wave packet is localized at the \( S_0 \) minimum. At positive time delays, after the pump has populated higher-energy excited states, the photoelectron signal shifts to higher energies, and its peak oscillates between 15.5 and 17 eV with an \( \sim 40 \text{ fs} \) period. This oscillatory behavior is highlighted in Fig. 4C, which displays a section of the signal at \( \epsilon_0 = 17.25 \text{ eV} \). Its Fourier transform, depicted in Fig. 4D, clearly shows a 120 cm\(^{-1}\) peak, associated with the main mode of the nuclear motion. To examine how the photoelectron signal is linked to the underlying molecular dynamics, we present

Fig. 3. Population and coherence dynamics of neutral uracil calculated for a 34-fs UV pump pulse centered at \( t = 0 \) and in resonance with the bright \( S_0 \) to \( S_2 \) transition. (A) The total populations in the (blue) \( S_0 \), (green) \( S_2 \), and (yellow) \( S_1 \) states show a population transfer from the \( S_0 \) to the \( S_2 \) states due to the pump pulse, a subsequent relaxation of the \( S_2 \) state, and the transfer of populations into the \( S_1 \) state due to the \( \text{CoIn} \) passage at around 100 fs. (B) Coherence between the \( S_0 \) and \( S_1 \) states generated at the \( \text{CoIn} \) passage.

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in Fig. 5 contour plots of the molecular wave packet at three representative time delays $T$ separated by 20 fs. The panels also show the corresponding value of the ionization energy $\omega_{A_0} (q)$ from the neutral $S_2$ to the ionic $D_0$ state. We see that the wave packet moves between regions in nuclear space associated with different ionization energies. These nuclear dynamics are encoded in the time dependence of the photoelectron signal in Fig. 4A. Additional spectral features, for example, at energies $\epsilon$ of 14 eV, are due to the other photoionization pathways, corresponding to the $D_1$ and $D_2$ excited states of the cation.

Fig. 4B depicts the coherence contribution $S_{coh}(\epsilon, T)$ (Eq. 16). The signal encodes the evolution of the $S_2/S_1$ coherence emerging during the CoIn passage at approximately $T = 100$ fs (see also Fig. 3). For this coherence term to contribute to the photoelectron signal, the pulse bandwidth has to be broader than the transition energy between states $S_2$ and $S_1$. Only then can the excitations be placed on the left and on the right branches of the loop diagram in Fig. 1 take place, corresponding to the two ionization pathways from different states $I$ and $I'$ to the ionic state $\alpha$. The coherence signal in Fig. 4B is very broad in energy as it is the sum of three ionization pathways to the three cationic states. Note that $S_{coh}(\epsilon, T)$ can be positive or negative, leading to an increase or decrease in the total photoelectron signal, respectively. This sign reflects the evolution and phase of the associated molecular coherence. Fig. 4B shows that the coherence contribution to the signal is weaker than that due to populations, reflecting the relative magnitude of the populations and coherences in Fig. 3. The emerging coherence between the $S_1$ and $S_2$ states is $\sim 1/100$ of the total populations. We stress that this ratio, albeit small, could be distinguished at the current experimental detection limit ($\approx 0.05\%$) (14). Furthermore, the 34-fs UV pump pulse used in this case was chosen to transfer populations without any optimization, but quantum-control techniques could be employed to optimize the pump pulse spectral and temporal features, and thus maximize the coherence contribution (42). Alternatively, molecules with more localized nuclear wave packets passing through the CoIn would exhibit a larger and longer-lived coherence and would thus enhance the coherence signature in the TRPES signal. The standard semiclassical approaches typically used to predict photoelectron spectroscopy signals (31−33) do not account for molecular coherences and thus miss these experimentally accessible signatures.

The role of coherences in TRPES is further highlighted in Fig. 6, which displays the total signal $S(\epsilon, T)$ and its two components $S_{pop}(\epsilon, T)$ and $S_{coh}(\epsilon, T)$ for an ultrashort probe pulse of $\tau = 200$ fs. The signal is displayed for time delays centered around $T = 0$ fs. Due to the very broad bandwidth of the attosecond probe pulse used, the photoelectron signal shows very broad lines with poor spectral resolution. The contributions of different neutral and ionic states, which could be distinguished in Fig. 4, are now convolved underneath the large probe pulse bandwidth. At the same time, the attosecond probe pulse employed here is broader than the transition energy between $S_0$ and $S_2$. Because of this, the total photoelectron signal in Fig. 6A contains clearly distinguishable signatures stemming from the coherence between these two states. This is further highlighted by comparing the population $S_{pop}(\epsilon, T)$ and coherence $S_{coh}(\epsilon, T)$ contributions in Fig. 6B and C, respectively. The $S_0/S_2$ coherence shown in the photoelectron signal is created during the pump excitation, in contrast to the more informative $S_1/S_2$ coherence created by the passage through the CoIn and discussed in Fig. 4. The wave packets in the $S_0$ and $S_2$ surfaces have a significant overlap, corresponding to a larger coherence than the one generated at the CoIn between $S_2$ and $S_1$. The amplitude of the $S_0/S_2$ coherence is comparable to the populations, leading to discernible features in the total photoelectron signal. We here assumed an ultrashort probe pulse with very good control over its jitter and arrival time. Thereby, $S_{coh}(\epsilon, T)$ allows one to follow the time dependence of this $S_0/S_2$ coherence and its oscillation between positive and negative values with high temporal resolution. The frequency of these fast coherence oscillations reflects the large transition energy between the $S_0$ and $S_2$ states.
Fig. 5. Evolution of the molecular wave packet in two-dimensional nuclear space. The black lines represent contour plots of the molecular wave packet at the three representative time delays $T$ indicated in each panel: (Top) $T = 37$ fs, (Middle) $T = 57$ fs, and (Bottom) $T = 77$ fs. The corresponding value of the ionization energy $(\omega_D(q) - \omega_S(q))$ from the neutral $S_2$ to the ionic $D_0$ state is displayed in the background of each panel.

High temporal and spectral resolution about CoIn dynamics from jittery, stochastic FEL pulses could also be obtained at the data-processing stage by a correlation analysis (19, 22) or machine learning (43), as recently proposed and investigated experimentally.

The good temporal resolution provided by the ultrashort probe pulse used in Fig. 6 can follow even the fast oscillations in the $S_2/S_0$ coherence. However, it does not offer high spectral resolution, rendering it difficult to separate and monitor coherences emerging from different sets of electronic states (41). Proposals to improve the temporal and spectral resolutions by means of trains of attosecond pulses have been made recently (44). Here, in order to retrieve the spectral information from temporally well-resolved data, in Fig. 7 we display the FROG spectrogram of the photoelectron signal $S(\epsilon_0, T)$ (Eqs. 1, 15, and 16) calculated for $\tau = 200$ fs and evaluated at $\epsilon_0 = 17.25$ eV. This spectrogram can be generated by a postprocessing analysis of the photoelectron signal $S(\epsilon_0, T')$ for a given $\epsilon_0$, by taking the Fourier transform

$$W(\omega_{\text{FROG}}, T) = \left| S(\epsilon_0, T') C_{\text{gate}}(T - T') e^{-i \omega_{\text{FROG}} T'} dT' \right|^2.$$  \[5\]

Here $C_{\text{gate}}(T) = e^{-T^2/(2 \tau_{\text{gate}}^2)}$ is a narrowband gate function used for data processing, with duration here set equal to $\tau_{\text{gate}} = 15$ fs, and does not require additional measurements. The energy $\epsilon_0$ was chosen so that it lies within the broad spectral peak of the photoelectron signal. Since the signal in Fig. 6 possesses very broad spectral features, one could have alternatively considered the FROG spectrogram of the energy-integrated signal, which would not require energy dispersion and could thus be more easily measured.

The spectrogram is shown in Fig. 7 within a relatively narrow region centered on $\omega_{\text{FROG}} = 0$ eV. Higher-frequency components, due, for instance, to the $S_2/S_0$ coherence, do not appear in this spectral region. The spectrogram of the total photoelectron signal is dominated by the slow evolution of the populations, which appear in Fig. 7A as a main peak.
thus dominate the spectrum at small values of $\omega$. The dynamics of the populations, which evolve slowly in time and increasing $\omega$, at $\tau$.

A contribution due to the packet evolution spanning the relevant regions in nuclear space.

The joint temporal and spectral resolution to monitor the wave across the CoIn passage is provided.

of the technique, key information about the spectral distribution could be similarly distinguished via frequency dispersion of the resolved ultrafast X-ray diffraction setup recently proposed in.

becomes clearly apparent. This is analogous to the frequency-allowed us to highlight the coherence contribution at sufficiently low spectral resolution. Valuable spectral resolution was retrieved by an analysis based on FROG spectrograms, which could be observed with existing spectrometers and could be enhanced by means of a suitably shaped pump pulse. For a shorter 200-as probe pulse, clear coherence signatures due to the wave packet overlap between the S$_2$ and S$_1$ surfaces were predicted. Attosecond pulses were shown to provide high temporal resolution of time-resolved photoelectron signals, at the expenses of lower spectral resolution. Valuable spectral resolution was retrieved by an analysis based on FROG spectrograms, which allowed us to highlight the coherence contribution at sufficiently large frequencies $\omega_{\text{FROG}}$.

Fig. 7. FROG spectrogram $W(\omega_{\text{FROG}}, T)$ (Eq. 5) of the time-resolved photoelectron signal $S(\epsilon_T, T)$ evaluated at $\epsilon_T = 17.25$ eV and obtained with a 20-eV probe pulse of duration $\tau = 200$ as. The FROG spectrogram is calculated assuming a Gaussian gate window of duration $\tau_{\text{gate}} = 15$ fs. (A) FROG spectrogram $W(\omega_{\text{FROG}}, T)$ of the total photoelectron signal, (B) FROG spectrogram $W_{\text{coh}}(\omega_{\text{FROG}}, T)$ of the coherence contribution $S_{\text{coh}}(\epsilon_T, T)$, and (C) sections of the (blue) total FROG spectrogram $W(\omega_{\text{FROG}}, T)$ in $A$ and of the (yellow) coherent contribution to the spectrogram $W_{\text{coh}}(\omega_{\text{FROG}}, T)$ in $B$ indicated values of $\omega_{\text{FROG}}$.

Advances in HHG- and FEL-based light sources are now providing ultrashort broadband pulses, opening up an entirely new regime of time-resolved investigations. We showed that experimentally detectable features appear in the time-resolved photoelectron signal, which are completely missed by the standard semiclassical formulation based on Fermi’s golden rule and require the inclusion of coherence contributions. Distinguishing these contributions in TRPES will provide a background-free probe of nonadiabatic dynamics, better indicative of CoIn than the contributions from state populations. Our simulations for uracil undergoing nonadiabatic dynamics highlight the key role of molecular coherences for future theory and experimental TRPES investigations.

Materials and Methods

Derivation of the Time-Resolved Photoelectron Signal. We consider a molecule initially in a neutral state, described by the Hamiltonian

$$H_{\text{neutral}} = \sum_{\alpha} \hat{H}_{\alpha} |\psi_{\alpha}\rangle \langle \psi_{\alpha}| + \sum_{\alpha \neq \beta} \hat{H}_{\alpha \beta} |\psi_{\alpha}\rangle \langle \psi_{\beta}|,$$

where $\alpha$ and $\beta$ label the adiabatic electronic states $|\psi_{\alpha}\rangle$ of the neutral molecule, and the operators $\hat{H}_{\alpha}$ and $\hat{H}_{\alpha \beta}$ act on the nuclear space. A probe pulse, centered at time $T$ as depicted in Fig. 1, ionizes the molecules, producing an ion with the Hamiltonian

$$H_{\text{ion}} = \sum_{\alpha} \hat{H}_{\alpha} |\varphi_{\alpha}\rangle \langle \varphi_{\alpha}| + \sum_{\alpha \neq \beta} \hat{H}_{\alpha \beta} |\varphi_{\alpha}\rangle \langle \varphi_{\beta}|,$$

where $\alpha$ and $\alpha'$ now label the adiabatic electronic states $|\varphi_{\alpha}\rangle$ of the ionic molecule, and $\hat{H}_{\alpha}$ and $\hat{H}_{\alpha \beta}$ act on the corresponding nuclear space. We neglect the effect of the Coulomb potential of the molecular ion on the free electron, which is thus described by the Hamiltonian

$$H_{\text{free}} = \sum_{k} \epsilon_{k} |\phi_{k}\rangle \langle \phi_{k}|,$$

where $k$ runs over the continuum states $|\phi_{k}\rangle$ of energy $\epsilon_{k} = k^2/2$. The photoionization process is described by the light-matter interaction Hamiltonian
\[ \hat{H}_{\text{int}} = -E(t-T) \cdot \hat{\Psi}^\dagger - E^*(t-T) \cdot \hat{\Psi}, \]

with the electric field \( E(t) = eE(t) = \epsilon E(t) e^{-i\omega t}, \) and the dipole operator in the rotating-wave approximation

\[ \hat{V} = \sum_{\alpha \beta} \hat{V}_{\alpha \beta}(t) \langle \phi_{\alpha} | \partial_t \phi_{\beta} \rangle, \]

Here \( \hat{V}_{\alpha \beta}(t) \) is a matrix element over the electronic degrees of freedom but is still an operator in the nuclear space of the neutral and ionic molecules. The photoelectron signal is defined as the integrated rate of change of the number \( N_e \) of photoelectrons with energy \( \epsilon \),

\[ S(\epsilon, t) = 2 \text{Im} \left\{ \int dt E(t-T) \sqrt{E} \int d\Omega_{ke} \sum_{\mu \nu} \left\{ \text{Tr} \left[ \hat{\Psi}_{\nu \mu, \alpha \beta}(t, t_0) | \phi_{\nu} \rangle \langle \phi_{\mu} | \phi_{\alpha} \right| (\hat{\Omega}^\dagger) (t) \right] \right\}. \]

Using Heisenberg's equations of motion and the interaction Hamiltonian in Eq. 9, we calculate the signal in Eq. 11, which gives

\[ S(\epsilon, t) = 2 \text{Re} \left\{ \int dt E(t-T) \sqrt{E} \int d\Omega_{ke} \sum_{\mu \nu} \left\{ \text{Tr} \left[ \hat{\Psi}_{\nu \mu, \alpha \beta}(t, t_0) | \phi_{\nu} \rangle \langle \phi_{\mu} | \phi_{\alpha} \right| (\hat{\Omega}^\dagger) (t) \right] \right\}. \]

Written in terms of the operators \( \hat{G}_{\alpha \beta}(t, t_0) \) acting on the nuclear space. The free evolution of a photoelectron \( | \phi_{\alpha} \rangle \) of energy \( \epsilon \) is given by the Green's function \( e^{-i(\epsilon - \omega)t} | \phi_{\alpha} \rangle \). The photoelectron signal can thus be recast as

\[ S(\epsilon, t) = 2 \text{Re} \left\{ \int dt E(t-T) \sqrt{E} \int d\Omega_{ke} \sum_{\mu \nu} \left\{ \text{Tr} \left[ \hat{\Psi}_{\nu \mu, \alpha \beta}(t, t_0) | \phi_{\nu} \rangle \langle \phi_{\mu} | \phi_{\alpha} \right| (\hat{\Omega}^\dagger) (t) \right] \right\}. \]

and can be partitioned into the sum of a population \( S_{\text{pop}}(r, t) (t \neq t' \) and a coherence contribution \( S_{\text{coh}}(r, t) (t = t') \). The evolution of the molecular wave packet \( \psi(t, q) \) was obtained by solving the Schrödinger equation for the neutral molecular surfaces \( \omega(q) \), where \( q \) is the vector of the nuclear coordinates considered in the model.

Furthermore, the Green's function \( G_{\alpha \beta}(q, t, t-t_0) \approx e^{-i\omega t} | \delta_{\alpha \beta} \rangle \rangle \) was approximated locally in terms of the ionic molecular surfaces \( \omega_{\alpha \beta}(q) \), assuming that its time dependence is slow compared to the duration of the ionizing pulse and that dynamics on different ionic potential energy surfaces are not coupled during this short pulse duration. With the above assumptions, the orientationally averaged population and coherence contributions to the photoelectron signal can be recast as

\[ S_{\text{pop}}(\epsilon, t) = 2 \text{Re} \left\{ \int dt \int d\Omega_{ke} \sum_{\mu \nu} \left\{ \text{Tr} \left[ \hat{\Psi}_{\nu \mu, \alpha \beta}(t, t_0) | \phi_{\nu} \rangle \langle \phi_{\mu} | \phi_{\alpha} \right| (\hat{\Omega}^\dagger) (t) \right] \right\}. \]

and

\[ S_{\text{coh}}(\epsilon, t) = 2 \text{Re} \left\{ \int dt \int d\Omega_{ke} \sum_{\mu \nu} \left\{ \text{Tr} \left[ \hat{\Psi}_{\nu \mu, \alpha \beta}(t, t_0) | \phi_{\nu} \rangle \langle \phi_{\mu} | \phi_{\alpha} \right| (\hat{\Omega}^\dagger) (t) \right] \right\}. \]

whereby, respectively, the unit vector \( i \) runs over the three directions \( x, y, \) and \( z \). The transition dipole matrix elements

\[ V_{\alpha \beta}(q) \equiv \langle \phi_{\alpha} | [\epsilon(q, r_1, \ldots, r_N)] \hat{\Psi}_{\beta} (r_1) \rangle \]

are defined in terms of the eigenstates of the neutral \( N \)- and ionic \( (N-1) \)-electronic systems. Due to the orthogonality between the cation and continuum electrons, the matrix element can be approximated as

\[ V_{\alpha \beta}(q) \approx \int d\epsilon \frac{e^{i\epsilon}}{\sqrt{2\pi\hbar^2}} \langle \phi_{\alpha} \hat{\Psi}_{\beta} \rangle (q, \epsilon) \]

in terms of the Dyson orbitals \( \phi_{\alpha \beta} \) in Eq. 2.

Data Availability. All study data are included in the article.

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