

Monitoring Ultrafast Nonadiabatic Dynamics in Molecules by Streaking of Photoelectrons

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Abstract: We demonstrate that time resolved photoelectron signals combined with photoelectron streaking provides a powerful tool for studying strongly coupled nuclear-electron dynamics in molecules.

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1. Introduction

Streaking of photoelectrons has been originally developed for the temporal characterization of attosecond extreme ultraviolet pulses [1–3]. When the time-resolved photoelectrons originate from a coherent superposition of electronic states, they carry an additional phase information, which can be retrieved by the streaking technique. In this contribution we extend the streaking formalism to include coupled electron and nuclear dynamics in molecules as well as initial coherences and demonstrate how it offers a novel tool to monitor non-adiabatic dynamics as it occurs in the vicinity of Conical intersection (CIs) and avoided crossings. Streaking can enhance the time resolution and provides direct signatures of electronic coherences, which affect many primary photochemical and biological events.

By combining time resolved photoelectron spectroscopy (TRPES) with the streaking technique, the phase of the molecular wave function may be recovered and the patterns of electronic coherences can be enhanced. This technique can be used as an alternative to stimulated Raman techniques [4] to detect electronic coherences created in the vicinity of CIs. During the passage through a CI the molecule is prepared in coherent super position of electronic and nuclear degrees of freedom. The pulse used to ionize the molecule covers at least a half cycle of the streaking field, coupling momentum states in the free electron wave packet. This introduces additional interference fringes that provide experimental signatures of electronic coherences.

2. Theory

Our derivation [5] extends the perturbative description of TRPES in the ionizing pulse [6] to take into account the free electron propagation under the influence of an IR streaking field as shown in Fig. 1(a). An initial pump-pulse prepares the system in a non-stationary state, which is subjected to an ionizing pulse. The ionizing field E_x and the streaking field E_s overlap temporally. The entire process is represented by the loop diagram [7] shown in Fig. 1(b).

The system is described by the Hamiltonian

$$H = H_M + H_x(t) + H_{es}(t), \quad (1)$$

which consists of the molecular Hamiltonian with bound neutral and ionic states (indexed by a and I respectively)

$$H_M = \hat{T} + \sum_a \hat{\epsilon}_a |a\rangle\langle a| + \sum_I \hat{\epsilon}_I |I\rangle\langle I|, \quad (2)$$

the minimal coupling Hamiltonian of the photoelectron in the presence of the streaking field

$$H_{es}(t) = \int d\mathbf{k} [\mathbf{k} - \mathbf{A}(t)]^2 \hat{c}_{\mathbf{k}} \hat{c}_{\mathbf{k}}^\dagger, \quad (3)$$

and the interaction between ionizing x-ray pulse and the matter

$$H_x = -E_x(t)(\hat{\mu} + \hat{\mu}^\dagger) \quad (4)$$

$$\hat{\mu}^\dagger = \int d\mathbf{k} \sum_{aI} \hat{c}_{\mathbf{k}}^\dagger |I\rangle\langle a| \hat{\mu}_{Ia}(\mathbf{k}).$$

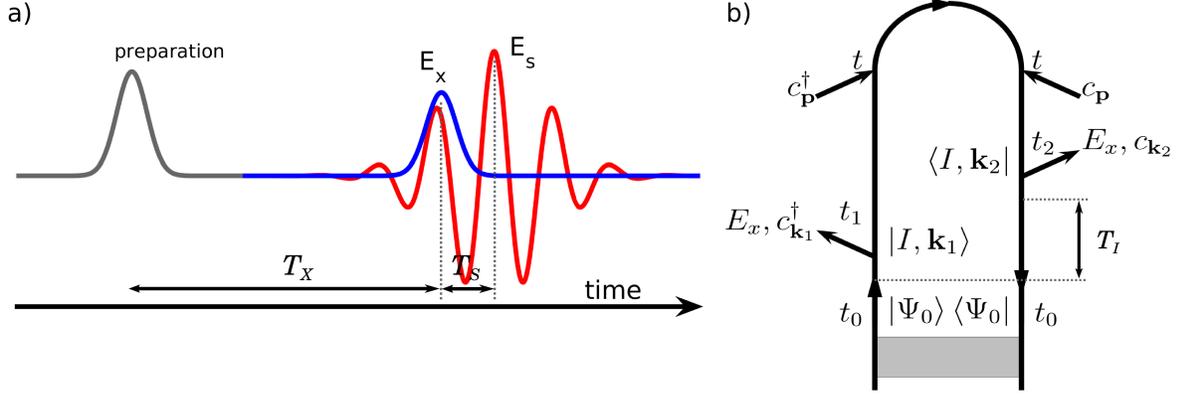


Fig. 1. (a) Pulse configuration for the streaked TRPES: An initial pulse prepares the molecule in a non-stationary superposition state followed, after a delay T_x , by an ionizing pulse E_x that has a temporal overlap with the streaking field E_s . (b) Loop diagram for the streaking process (Eq. 5). The length of the time interval T_I is determined by the matter evolution and represents the time it takes for ionization to take place. The photoelectrons are detected in momentum states $|\mathbf{p}\rangle$ at time t after the time evolution in the streaking field E_s .

where μ_{Ia} is the transition dipole moment between the neutral and ionic state, \hat{T} is the kinetic energy operator of the nuclei, and the potential energy operators of the molecular electronic states are given by $\hat{\epsilon}_a$, $\mathbf{A}(t) = -\int_{-\infty}^t dt' \mathbf{E}_s(t')$ is the vector potential of the streaking field, and $\hat{c}_{\mathbf{k}}^\dagger$ is the creation operator of a photoelectron with kinetic momentum \mathbf{k} . Here, $\hat{c}_{\mathbf{k}}^\dagger$ are fermionic operators acting in the photoelectron space while $\hat{\epsilon}_a(t)$ and $\hat{\mu}_{Ia}(\mathbf{k})$ are operators in the nuclear subspace.

The signal is given by the expectation value at the detection time t of the photoelectron number operator $\hat{N}_{\mathbf{p}}$. This depends on the kinetic momentum \mathbf{p} , the central time of the x-ray pulse T_x , and the streaking field parameters $\Lambda_s \equiv (T_s, \sigma_s, \omega_s, \phi_s)$. Expanding $\hat{N}_{\mathbf{p}}$ to second order in E_x , as depicted in Fig. 1(b), yields our key result:

$$S_e(\mathbf{p}, T_x, T_s) \approx \int dt_1 \int dt_2 \tilde{E}_x^*(t_1 - T_x) \tilde{E}_x(t_2 - T_x) C_M(t_2, t_1) e^{-i(\frac{p^2}{2} - \omega_x)(t_2 - t_1)} \exp \left[-i\mathbf{p} \int_{t_1}^{t_2} d\tau \tilde{\mathbf{A}}(\tau + T_s - T_x) \right] \quad (5)$$

$$C_M(t_2, t_1) = \langle \Psi_0 | U_M^\dagger(t_2, t_0) \mu(\mathbf{p} - \mathbf{A}(t_2)) U_M^\dagger(t_2, t_1) \mu(\mathbf{p} - \mathbf{A}(t_1)) U_M(t_1, t_0) | \Psi_0 \rangle \quad (6)$$

The dynamical effects of the molecular bound states are contained in the correlation function C_M (a tilde indicates shifted field envelopes centered at zero argument). The molecular propagator U_M represents the full nuclear+electronic molecular Hamiltonian including non-adiabatic couplings. We have assumed that the photoelectron wavepacket does not interact with the molecular ion, which is reasonable for sufficiently fast photoelectrons [8]. The streaking field must be weak enough to not perturb the molecular eigenstates or ionize the molecule, which also justifies dropping the \mathbf{A}^2 interaction in the minimal coupling Hamiltonian (Eq. 3), as done in Eq. 5. The initial state $|\Psi_0\rangle$ is given by a product of a non-stationary molecular state and the photoelectron vacuum state. T_x and T_s are the times of the x ray ionization and streaking pulse as shown in Fig. 1 and E_p is the photoelectron kinetic energy. Note that the signal may not be recast as a modulus square of a transition amplitude and may not be generally inverted by a FROG algorithm.

3. Detection of Nonadiabatic Dynamics

We demonstrate the signatures of nonadiabatic dynamics in the signal for a molecular model with two vibrational modes and a CI. The model has two electronic states, and two ion state potential energy surfaces (see [6] for details). The wave packet reaches the conical intersection at ≈ 10 fs, creating an electronic coherence by branching onto the two electronic surfaces.

A set of streaking spectra resulting from the dynamics is shown in Fig. 2. The ionization pulse length used (5 fs FWHM) is not capable of resolving the coherent beating pattern in a bare PES (Fig. 2(a)). However, the application

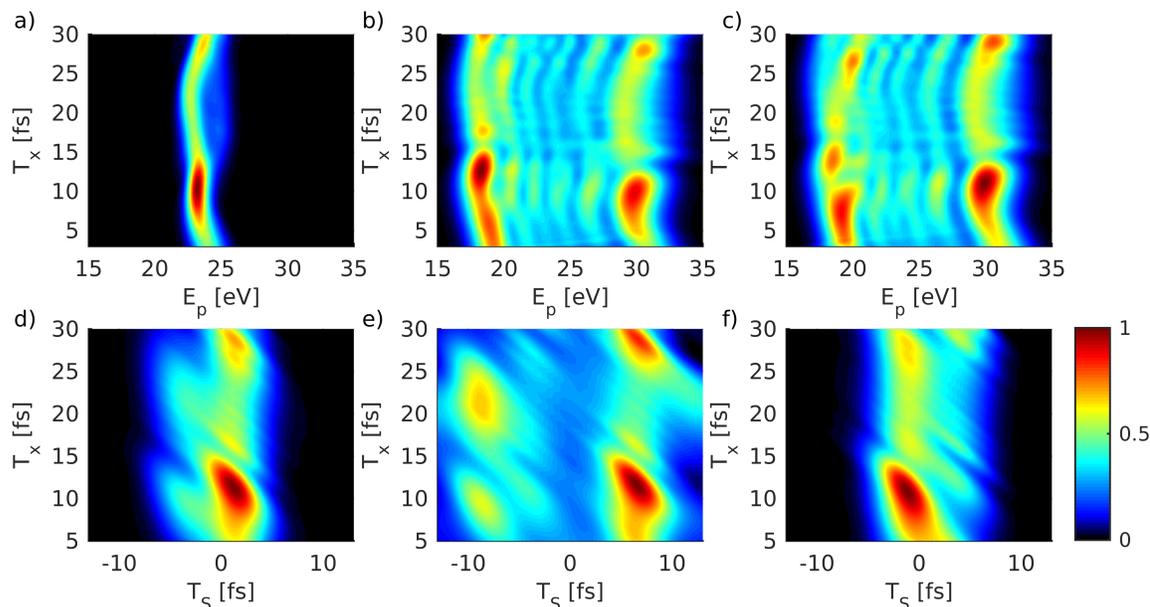


Fig. 2. Normalized photoelectron signals for the molecular 2D CI model with parameters $(\sigma_s, \sigma_x) = (8.0, 5.0)$ fs, $(\omega_s, \omega_x) = (0.82, 20)$ eV. TRPES without (a) and with streaking field ((b) $T_s = 0$ fs, (c) $T_s = -1.2$ fs). Streaking delay vs. ionization delay for $E_p = (18.2, 21.6, 29.7)$ eV ((d), (e), and (f) respectively).

of the streaking pulse (Fig. 2(b) and (c), different streaking delays) shows how the streaking field distributes the photoelectrons along E_p into the streaking side bands. The interference between the sidebands is sensitive to the phase of the electronic superposition, allowing to identify the built up coherence due to the CI. Comparison of Fig. 2(b) and (c) shows that for different delays of the streaking pulse the pattern varies for times where an electronic coherence is present ($T_x > 10$ fs). The PES is stretched along E_p thus effectively increasing the time resolution by distributing the photoelectrons over E_p according to their release time. Figures 2(d)-(f) display the photoelectron signal in dependence of the ionization delay T_x and the streaking delay T_s for different values of E_p . This representation makes it clear that streaking puts a time stamp on the photoelectrons. The pattern is not symmetric with respect to T_s as it would be for an atom [5]. This is due to the nuclear motion – electrons released at different times originate from different nuclear configurations. The beating pattern along T_x appears at around 10 fs and creates lines on the diagonal T_x/T_s as clear indicator of the electronic coherence created by the CI.

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