

## Monitoring Nonadiabatic Electron-Nuclear Dynamics in Molecules by Attosecond Streaking of Photoelectrons

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(Received 4 May 2016; published 22 July 2016)

Streaking of photoelectrons has long been used for the temporal characterization of attosecond extreme ultraviolet pulses. When the time-resolved photoelectrons originate from a coherent superposition of electronic states, they carry 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. We demonstrate how streaked photoelectrons offer a novel tool for monitoring nonadiabatic dynamics as it occurs in the vicinity of conical intersections and avoided crossings. Streaking can provide high time resolution direct signatures of electronic coherences, which affect many primary photochemical and biological events.

DOI: 10.1103/PhysRevLett.117.043201

*Introduction.*—The rates and outcomes of virtually all photochemical and photobiological processes are dominated by conical intersections (CIs) [1–4], which provide a fast sub-100-femtosecond nonradiative pathway back to the ground state. At a CI, the electronic and nuclear degrees of freedom frequencies are comparable and strongly mix due to the breakdown of the Born-Oppenheimer approximation. Available techniques for the detection of CIs include the optical monitoring of excited-state populations [1,5,6], vibrational spectra [7–10], electronic Raman techniques [11,12], and photoelectron spectroscopy (PES) [13–15]. Attosecond pulse sources [16–21] can directly access the electron dynamics of molecular systems [22–24]. This opens up the possibility of probing CIs by measuring the electronic coherences they generate.

PES [25] is a well established technique for exploring the electronic structure of molecules and solid-state systems [26]. Its time-domain extension, time-resolved PES (TRPES) [27,28], is further capable of following the nuclear dynamics on excited-state potential energy surfaces. Signatures of electronic coherences and nonadiabatic dynamics can be detected through temporal oscillations on top of the conventional photoelectron signal [14,15]. Typical energy gaps between molecular valence states span a range of a few eV. Subfemtosecond pulses are thus necessary to resolve the beating pattern in the time domain. By exposing the generated photoelectrons to another strong infrared (IR) field, effectively modifying their kinetic energy, streaking can be used to detect their time of release from the bound states [29,30]. This method was originally developed to characterize the shape of attosecond extreme ultraviolet (XUV) pulses [31–33]. The applied few-cycle IR pulse acts as a gate for the photoelectrons, commonly referred to as streaking. It has been used to extract the quantum phase of the underlying wave function in atoms [34], the time delay in tunnel

ionization processes [35–37], or the generation of ultrafast electron pulses [38].

In this Letter, we extend the theory of TREPS to include nonadiabatic electron and nuclear dynamics in molecules. We demonstrate that by combining TRPES with the streaking technique, the phase of the molecular wave function may be recovered by the application of a few-cycle streaking field. The patterns of electronic coherences already found in unstreaked TRPES can be enhanced by the streaking field, thus improving the temporal resolution. This can be used as an alternative to stimulated Raman techniques [11], which were recently proposed for the detection of molecular electronic coherences created at CIs. Unlike a conventional streaking setup, the system is prepared in a coherent superposition of electronic and nuclear degrees of freedom which must be described in the joint electronic and nuclear phase space. The pulse used to subsequently ionize the molecule covers at least half a cycle of the streaking field. This couples the momentum states in the free electron wave packet originating from different molecular states and introduces additional interference fringes attributable to electronic coherence.

*Streaking: Theory and schematics.*—Our derivation extends the perturbative description of TRPES in molecules [14] 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 nonstationary 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 [39] 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)

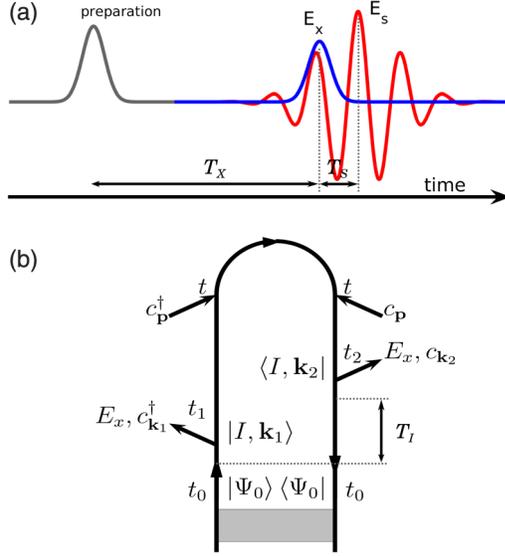


FIG. 1. (a) Pulse configuration for the streaked TRPES. An initial pulse prepares the molecule in a nonstationary superposition state followed, after a delay  $T_x$ , by an ionizing pulse  $E_x$  that has a temporal overlap with the streaking field  $E_s$ . (b) Loop diagram for the streaking process [Eq. (6)].  $\Psi_0$  represents the arbitrary molecular electron and nuclear wave packet prepared by optical excitation. The length of the time interval  $T_I$  is determined by the matter evolution in Eq. (7) 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.

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

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 the ionizing x-ray pulse and the matter

$$H_x = -E_x(t)(\hat{\mu} + \hat{\mu}^\dagger) \\ \hat{\mu}^\dagger = \int d\mathbf{k} \sum_{al} \hat{c}_{\mathbf{k}}^\dagger |I\rangle \langle a| \hat{\mu}_{Ia}(\mathbf{k}), \quad (4)$$

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

$$S(\mathbf{p}, T_x, \Lambda_s) = \langle \hat{N}_{\mathbf{p}} \rangle(t). \quad (5)$$

Expanding Eq. (5) to second order in  $E_x$ , as depicted in Fig. 1(b), yields our key result,

$$S_e(\mathbf{p}, T_x, T_s) \approx \int dt_1 \int dt_2 \tilde{E}_x^*(t_1 - T_x) \tilde{E}_x(t_2 - T_x) \\ \times C_M(t_2, t_1) e^{-i((\mathbf{p}^2/2) - \omega_x)(t_2 - t_1)} \\ \times \exp \left[ -i\mathbf{p} \int_{t_1}^{t_2} d\tau \tilde{\mathbf{A}}(\tau + T_s - T_x) \right] \quad (6)$$

$$C_M(t_2, t_1) = \langle \Psi_0 | U_M^\dagger(t_2, t_0) \mu(\mathbf{p} - \mathbf{A}(t_2)) U_M^\dagger(t_2, t_1) \\ \times \mu(\mathbf{p} - \mathbf{A}(t_1)) U_M(t_1, t_0) | \Psi_0 \rangle. \quad (7)$$

The 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  $U_M$  depends on the full nuclear + electronic molecular Hamiltonian including nonadiabatic couplings. We have assumed that the photoelectron wave packet does not interact with the molecular ion, which is reasonable for sufficiently fast photoelectrons [40]. 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 is done in Eq. (6). The initial state  $|\Psi_0\rangle$  is given by a product of a nonstationary molecular state and the photoelectron vacuum state. When the nuclear degrees of freedom are neglected, Eq. (6) reduces to the modulus squared of an amplitude [34] and can be recast as a frequency-resolved optical gating trace, which allows the inversion of signals to yield the ionization pulse shape or the quantum phase of the atomic state [for a detailed derivation, see the Supplemental Material [41]]. However, more generally, the nuclear and electronic degrees of freedom are coupled and the matter correlation function  $C_M$  depends in a nontrivial way on the propagation of the molecular wave packet in the interval  $T_I = [t_1, t_2]$ , where the ionization takes place (see Fig. 1). The precise definition of the ionization time and its detection has drawn considerable attention [35–37]. The time dependence, via the nuclei, of the electronic eigenvalues is the main difference from atomic experiments. In the limit of an impulsive ionization event  $T_I \rightarrow 0$  and Eq. (6) captures a snapshot of the system that depends on  $T_x$  and  $T_s$ . When the ionization event duration  $T_I$  is long enough to allow for nuclear motion, the signal also depends on the time evolution during the  $T_I$  interval where there is a

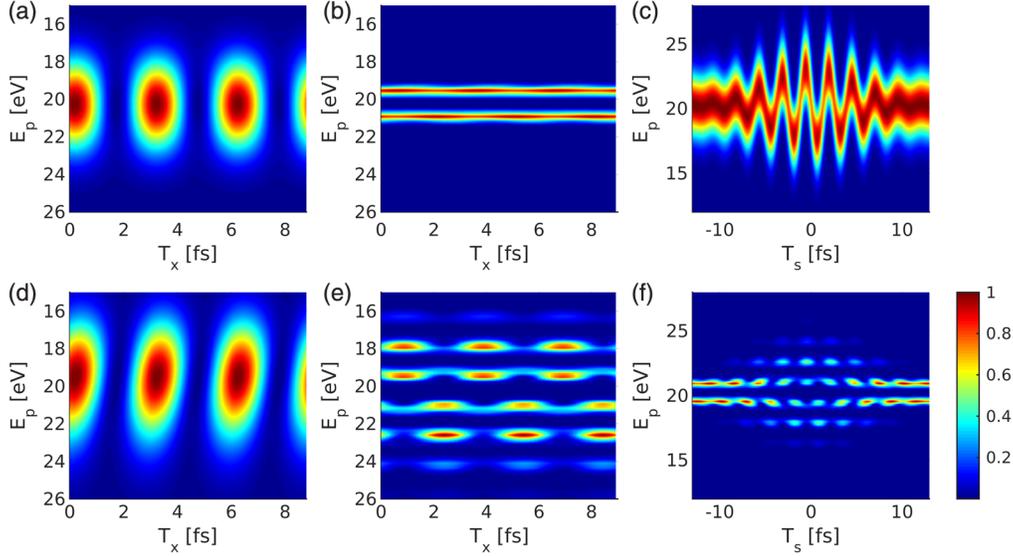


FIG. 2. Comparison of TRPES in a purely electronic (atomic) system for different pulse parameters. (a)  $\sigma_x = 0.5$  fs. The beating caused by the coherence is well resolved in the time domain. (b)  $\sigma_x = 5.0$  fs. Time resolution is lost. (d) Like (a), but with the streaking field applied (no major effect in this case). (e) Like (b), but with the streaking field applied, and the resolution is recovered. (c) Streaking with  $\sigma_x = 0.5$  fs recovers the structure of the streaking field itself, while (f)  $\sigma_x = 5.0$  fs creates interference sidebands.

coherence between the electronic states of the neutral molecule [see Fig. 1(b)]. The evolution during  $T_I$  is given by Eq. (7). The propagator  $U_M^\dagger(t_1, t_2)$  describes the evolution of the nuclear wave packet on the potential energy surface of the ionic state.

To set the stage, we first present the basic features of the streaked PES with initial coherence for a purely electronic atomic model system in order to illustrate the signatures of purely electronic coherence in the streaking signal. The molecular system with the coupled electron and nuclear dynamics is discussed in the next section. We assume a two level atom with bound states  $|g\rangle$  and  $|e\rangle$ ,  $\omega_e - \omega_g = 1.36$  eV, and a single ion state with ionization energies  $(\omega_{I_g}, \omega_{I_e}) = (5.44, 4.08)$  eV. The oscillation period attributable to the coherence in the streaking field-free PES is  $\approx 3$  fs, setting an upper bound to the ionization pulse length for the observation of the beating pattern in a conventional TRPES experiment. The system is prepared initially in a coherent superposition of  $|g\rangle$  and  $|e\rangle$  and is subsequently ionized by an XUV Gaussian pulse with an  $\omega_x = 25$  eV central frequency and  $\sigma_x$  [full width at half maximum (FWHM)] duration:

$$\tilde{E}_x(t) = E_x e^{-t^2/0.72\sigma_x^2} \quad (8)$$

The streaking field vector potential is given by

$$\tilde{\mathbf{A}}(t) = \mathbf{E}_s \int_{-\infty}^t d\tau \cos(\omega_s \tau + \phi_s) e^{-\tau^2/0.72\sigma_s^2}, \quad (9)$$

where  $\omega_s$  is its carrier frequency and  $\phi_s$  the carrier envelope phase. Figures 2(a) and 2(b) show the bare, unstreaked PES for two ionization pulse lengths. The FWHM of the

ionization pulse used in Fig. 2(a) is 0.5 fs and can temporally resolve the beating pattern. However, the states  $|g\rangle$  and  $|e\rangle$  cannot be distinguished along the  $E_p$  axis due to the broad width of  $E_x$ . The longer ionization pulse 5 fs used in Fig. 2(b) allows for a clear resolution of states  $|g\rangle$  and  $|e\rangle$  in the frequency domain but is too long to resolve their time-domain beating pattern. Figures 2(d) and 2(e) show the PES under the influence of a streaking field ( $T_s = 0$ ,  $\sigma_s = 8$  fs,  $\omega_s = 1.6$  eV,  $\phi_s = 0$ ) for  $\sigma_x = 0.5$  fs and  $\sigma_x = 5$  fs, respectively. The beating pattern is recovered by the spreading of the photoelectron peaks in Fig. 2(e), where the sidebands are generated at  $E_p = \epsilon_{a/b} \pm n\omega_s$  for an integer  $n \geq 1$ . Typical streaking spectra are shown in Figs. 2(c) and 2(f). With an ionization pulse length shorter than the optical cycle of the streaking field [Fig. 2(c)], the pattern of the streaking field is recovered. However, the two states may not be resolved by the photoelectron energy. For an ionization pulse length covering a full optical cycle of the streaking field [Fig. 2(f)], the frequency resolution is

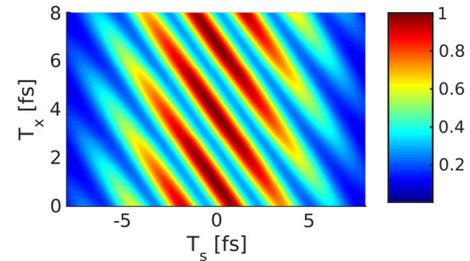


FIG. 3. Streaking signal in purely electronic atoms vs the ionization and streaking pulse delay. The diagonal pattern is caused by the coherences.

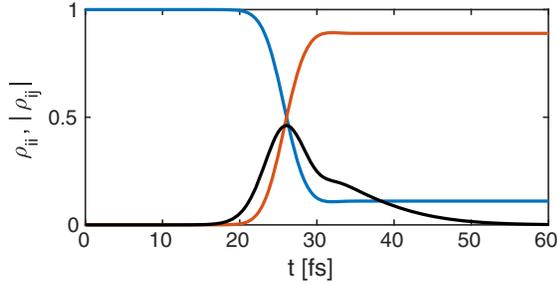


FIG. 4. Time evolution of the electronic populations [(blue) state  $a$  and (red) state  $b$ ] for the one-dimensional molecular model. The magnitude of the electronic coherence ( $\rho_{ab} = \langle \phi_a | \phi_b \rangle$ ) is indicated by the black curve. At  $\approx 20$  fs the molecule hits the avoided crossing.

retained. The pattern in the photoelectron kinetic energy  $E_p$  is generated by the sidebands in ( $E_p = \epsilon_{a/b} \pm n\omega_s$ ), while the oscillatory pattern in  $T_s$  is a clear signature of the coherence. An eigenstate or an incoherent mixture of two states would not show the beating pattern; i.e., we would see straight lines along  $T_x$ .

Figure 3 shows the signal vs  $T_x$  and  $T_s$  at a fixed  $E_p = 18$  eV. This representation can be used as an indicator for the initial coherence: The diagonal pattern is caused by the quantum phase of the superposition (i.e., the time dependence of the beating pattern). In the case of incoherent states, the signal is independent of  $T_x$ , yielding a purely vertical pattern. This clearly shows the capability of regaining time resolution when the streaking sidebands of the two states coincide ( $\epsilon_a \pm n_a\omega_s = \epsilon_b \pm n_b\omega_s$ ).

*Streaking detection of nonadiabatic dynamics.*—We now demonstrate the signatures of nonadiabatic dynamics in the

signal using a harmonic model with a single vibrational mode. The model has two electronic states, represented by two symmetrically displaced harmonic oscillators, a Gaussian diabatic coupling, and a harmonic ion state (for details of the model, see the Supplemental Material [41]). The quantum dynamics simulation starts out with a displaced Gaussian wave packet as its initial condition and hits the curve crossing at  $\approx 20$  fs, creating an electronic coherence (see Fig. 4). This simple model can be solved exactly using a numerical grid (see the Supplemental Material [41]).

A set of streaking spectra resulting from the dynamics is shown in Fig. 5. The ionization pulse length used (5 fs FWHM) is not capable of resolving the coherent beating pattern in a bare PES [Fig. 5(a)]. However, the application of the streaking pulse [Fig. 5(d)] shows a clear signature of coherent oscillations for  $T_x > 20$  fs (i.e., after the molecule has reached the avoided crossing). 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. The typical streaking representation ( $E_p$  vs  $T_s$ ) is shown in Figs. 5(b) and 5(e) for different ionization delays  $T_x$ . The pattern of the streaking pulse is blurred since the ionization pulse covers more than a full cycle of the streaking field. The representation in Figs. 5(c) and 5(f) makes it clear that streaking puts a time stamp on the photoelectrons. The beating pattern along  $T_x$  appears at around 30 fs and creates lines on the diagonal  $T_x/T_s$  as a clear indicator of the electronic coherence created by the avoided crossing. Unlike Fig. 3, the pattern is not symmetric with respect to  $T_s$ . This is because of the nuclear motion: Electrons released at different times originate from different nuclear configurations.

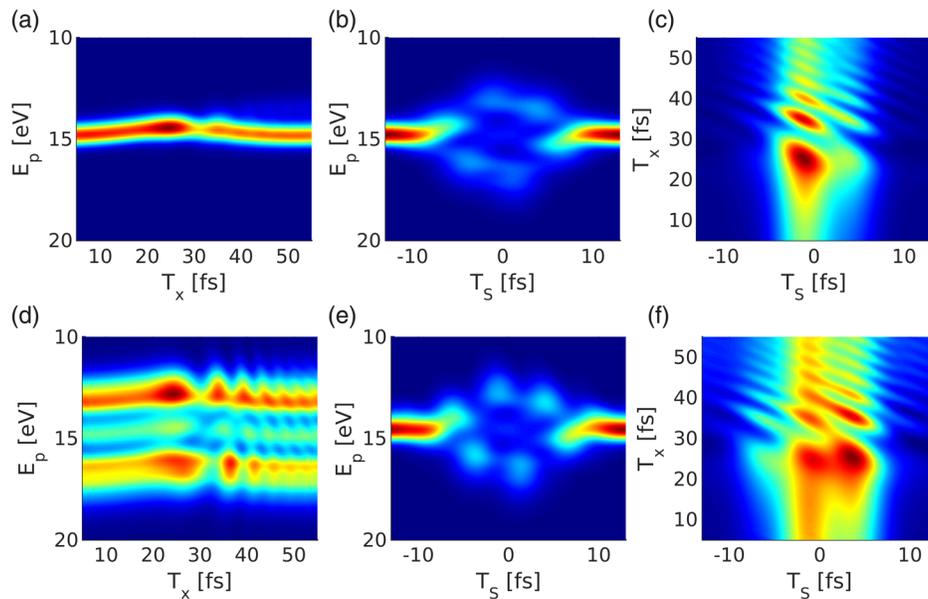


FIG. 5. Streaking spectra for the molecular one-dimensional model (as described in the Supplemental Material [41]) with parameters  $(\sigma_s, \sigma_x) = (8.0, 5.0)$  fs,  $(\omega_s, \omega_x) = (0.82, 20)$  eV. TRPES (a) without and (d) with a streaking field ( $T_s = 0$ ). Photoelectron energy vs streaking delay for (b)  $T_x = 7$  fs and (e)  $T_x = 35$  fs. Streaking delay vs ionization delay for (c)  $E_p = 12$  eV and (f)  $E_p = 13$  eV.

*Conclusions.*—We have extended the description of TRPES in molecules to account for the effect of an IR streaking field. This strong field couples the momentum states of the free electron wave packet and thus allows the recovery of the electronic coherences imprinted in it with a higher resolution than that of bare TRPES. The streaking field clocks the photoelectron release time by spreading them over a range of kinetic energies. These features are routinely used to characterize attosecond pulses for a given atomic matter dynamics. Here, we demonstrate that a reverse objective can be met—i.e., measurement of the matter dynamics knowing the pulses—and that it can be extended to nonadiabatic molecular systems.

It becomes clear that the streaking field could be used to detect avoided crossings and conical intersections in molecules. In the presence of nuclear dynamics, the signal may no longer be recast as an amplitude squared since the wave packet evolves nontrivially between the two interactions with the ionization x-ray pulse. This evolution is responsible for the loss of symmetry along  $T_s$  in the streaking spectra and can be used to infer and quantify the underlying nuclear dynamics.

The support of the Chemical Sciences, Geosciences, and Biosciences division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy through Award No. DE-FG02-04ER15571 and of the National Science Foundation (Grant No. CHE-1361516) is gratefully acknowledged. S.M. further thanks the Feiburg Institute of advanced studies (FRIAS) for providing a stimulating environment that greatly facilitated this work. K. B. was supported by the DOE award. M. K. gratefully acknowledges support from the Alexander von Humboldt Foundation through the Feodor Lynen program.

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