Stimulated X-ray Raman Imaging of Conical Intersections
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Supporting Information

ABSTRACT: The conical intersection dynamics of thiophenol is studied theoretically using the stimulated X-ray Raman imaging (SXRI) technique. SXRI employs a hard X-ray narrowband/broadband hybrid probe field and provides a real-time and real-space image of the passage through conical intersections. The signal, calculated using the minimal-coupling radiation/matter Hamiltonian, carries the phase information, and the real-space image of the transition charge density can be reconstructed by its Fourier transform. The two conical intersections (S₁/S₀ (1⁺ππ*/1⁻πσ*) and S₂/S₀ (1⁻πσ*/S₀)) can be distinguished and identified by the diffraction patterns in the level crossing regimes.

Nonadiabatic dynamics where the Born–Oppenheimer approximation breaks down is important in many photochemical reactions.1 Nonadiabatic effects become strong at conical intersections (CIs), where two or more electronic surfaces become energetically degenerate and the coupling between the electronic and nuclear degrees of freedom are strong, as their time scale separation no longer holds. CIs provide effective and ultrafast nonradiative electronic decay channels for excited molecules. CIs play a key role in many chemical and biophysical processes, such as internal conversion, intersystem crossing, charge transfer, photoisomerization, and photodissociation.2−8 Probing and characterizing CIs has been a primary goal for understanding photochemical reactions. Several techniques for probing conical intersections have been proposed based on monitoring state populations,9,10 transient vibrational/visible spectra,11−15 and photoionization spectra.16 The direct unambiguous experimental observation of CIs in molecules is an open challenge. Spectroscopic techniques that probe an intrinsic property of CIs, such as electronic coherence, strong transition dipole moment, zero electronic energy, and nuclear energy are necessary.

In this paper, we propose a stimulated X-ray Raman imaging (SXRI) technique for monitoring the real-time and real-space imaging of the transition charge density at the CI. So far, stimulated X-ray diffraction has not been realized experimentally but has been predicted theoretically (sum-frequency-generation diffraction)16 and should be feasible with intense free electron laser sources. An electronic coherence is created at the CI in the course of the nonadiabatic dynamics. A hybrid X-ray probe field composed of femtosecond narrowband (probe) and attosecond broadband (stimulated emission) pulses then provides a space-resolved image of the electronic coherence at the CI thanks to the short wavelength of the X-ray probe field. The signal does carry phase information,16−19 and the real-space image of the transition charge density can be reconstructed by its Fourier transform. The resulting real-time movie20−23 monitors the real-space image of the charge density. Conventional diffraction measurement, in contrast, provides the modulus square of the charge density and misses all phase information. This is known as the crystallographic phase problem.24,25 The SXRI technique provides a background-free probe for CIs. We apply the technique to probe CI dynamics in the photodissociation of the S−H bond in thiophenol after an excitation by XUV light to the S₁ (1⁺ππ*) state (See Figure 1). Earlier studies have shown two conical intersections, CI-1 (S₁/S₀ (1⁺ππ*/1⁻πσ*) crossing) and CI-2 (S₁/S₀ (1⁻πσ*/S₀) crossing) depicted in Figure 1c serve as nonadiabatic relaxation channels.3,26−29 We employed the surface hopping classical trajectory method30,31 to simulate the conical intersection dynamics of thiophenol. The transition charge density variation across the CIs is monitored in real-time and real-space using the stimulated X-ray diffraction patterns calculated here.

THE SXRI SIGNAL

Figure 1 shows (a) the SXRI setup, (b) the corresponding diagram, and (c) the energy level scheme for the SXRI signal. A preparation process (gray box) creates a nuclear wavepacket in the lal exited state launching the nonadiabatic dynamics at time delay T = 0 (see Figure 1c for the notation for electronic states). Electronic coherence is created only as the wavepacket approaches the CI and is not created by the initial preparation (ρ_{0b}(T = 0) = 0). A hybrid probe pulse composed of a hard X-ray narrowband femtosecond pulse A_{0} and a hard X-ray broadband attosecond pulse A_{1} then generates the SXRI signal.23

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signal at time delay \( T \). The narrowband pulse \( \mathcal{A}_0 \) scatters off the real-space charge density \( \sigma(r,t) \) of a molecule after time delay \( T \) following the arbitrary preparation (gray box) of an initial nonstationary electronic population state at \( T = 0 \), where \( \mathbf{k}_i \) is the wave-vector of the signal field. The signal field emission is then stimulated by a broadband pulse \( \mathcal{A}_i \). The signal at time delay \( t \) is the wave-vector of the signal field. The scattered signal (see eq 10) is recorded by \( \mathcal{A}_0 \).

Figure 1. (a) Pulse configuration for the SXRI technique, (b) ladder diagram, and (c) energy level scheme with schematic diabatic potential energy surface along the S-H bond distance. A narrowband femtosecond X-ray pulse \( \mathcal{A}_0 \) scatters off the real-space charge density \( \sigma(r,t) \) of a molecule after time delay \( T \) following the arbitrary preparation (gray box) of an initial nonstationary electronic population state at \( T = 0 \), where \( \mathbf{k}_i \) is the wave-vector of the signal field. The signal field emission is then stimulated by a broadband pulse \( \mathcal{A}_i \). The signal at time delay \( t \) is the wave-vector of the signal field. The scattered signal (see eq 10) is recorded by \( \mathcal{A}_0 \).

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The SXRI signal was calculated using the minimal-coupling Hamiltonian for the radiation–matter interaction which in the off-resonant regime reads

\[
\hat{H}_{\text{int}} = \frac{1}{2} \int dt \hat{\sigma}(r) \hat{A}_i(r,t) \hat{A}_0^\dagger(r,t)
\]

(1)

where \( \hat{\psi}^{\dagger}(r) \) is the creation operator for the photon field modes. The SXRI signal was calculated using the minimal-coupling Hamiltonian for the radiation–matter interaction which in the off-resonant regime reads

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(1)
\[ S(\omega, Q, T) = \int dt e^{i\omega(t-T)} \mathcal{A}_1(\omega) \mathcal{A}_0(t-T) \times \sum_{\alpha, \beta} \rho_{\alpha\beta}(t) \sigma_{\alpha\beta}(Q, t) \]
\[
= \int dt e^{i\omega(t-T)} |\mathcal{A}_1(\omega)||\mathcal{A}_0(t-T)| \sum_{\alpha, \beta} |\rho_{\alpha\beta}(t)| \times \sigma_{\alpha\beta}(Q, t)e^{i\phi_{\alpha\beta} - \phi_{0\beta} + \phi_{0\alpha}} \]

(10)

where \( \rho_{\alpha\beta}(t) = |\rho_{\alpha\beta}(t)|e^{i\phi_{\alpha\beta}} \) is the matrix element of the many-body electronic density matrix in adiabatic basis, \( \phi_{\alpha\beta}(t) \) is a time-dependent phase of the density matrix element, \( \mathcal{A}_1(\omega) = |\mathcal{A}_1(\omega)|e^{i\phi} \), and \( \mathcal{A}_0(t) = |\mathcal{A}_0(t)|e^{i\phi} \) where \( \phi \) is the phase of the \( \mathcal{A} \) field. The charge density \( \mathcal{A}(\mathbf{r}, t) \) can be retrieved by inverse Fourier transform of \( \langle \mathcal{A}(\mathbf{Q}, t) \rangle \), which can be obtained by deconvolution of the three-dimensional SXRI signal. The time-dependence of \( \sigma_{\alpha\beta}(\mathbf{r}, t) \) and \( \sigma_{\alpha\beta}(\mathbf{Q}, t) \) arises from the nuclear dynamics. The signals presented in Figures 4 and S1 are calculated using eq 10 for \( \phi_0 \) - \( \phi_1 = 0 \). Because the signal is linear in the probe field amplitudes \( \mathcal{A}_1, \mathcal{A}_0 \), it carries the phase factor \( e^{i(\phi_0 - \phi)} \). Controlled phases \( \phi_0 \) - \( \phi_1 \) are required to generate a finite SXRI signal; the signal vanishes upon averaging over a random phase probe pulse. Note that when the two probe field phases are the same, \( \phi_0 = \phi_1 \), the phase of the electronic coherence \( \rho_{\alpha\beta}(t) \) can be directly measured by the signal. The signal from populations (diagonal elements, \( \rho_{\alpha\alpha} \)) vanishes because it has no dynamical phase \( \phi_{\alpha\alpha}(t) = 0 \). The SXRI signal therefore provides a background-free image of the electronic coherences \( \rho_{\alpha\beta} \) created in the vicinity of the CI. Frequency-resolved stimulated Raman resonance between the wavepacket on two surfaces may allow detection of the time-resolved energy splitting and the potential energy surface gradient in coordinate space.

SXRI is an extension of the TRUECARS (transient redistribution of ultrafast electronic coherences in attosecond Raman signals) technique,33 which can probe the conical intersection in real-time with a stimulated Raman probe. The difference is that by using hard X-rays, we obtain an image of the transition charge density. This requires working with the minimal-coupling Hamiltonian for the radiation–matter interaction.

**SURFACE HOPPING NONADIABATIC DYNAMICS OF THIOPHENOL**

Modeling the strongly coupled electronic and nuclear degrees of freedom in photochemical reactions is a computational challenge. Simulation protocols that go beyond the Born–Oppenheimer approximation include (multiconfigurational) Ehrenfest dynamics,34 multiconfigurational time dependent Hartree,35 multiple spawning,36 and semiclassical approaches, which treat the electrons quantum mechanically and the nuclear degrees of freedom classically and provide a practical level of theory to describe nonadiabatic dynamics in polyatomic molecules. Surface hopping37,38 is the most commonly used semiclassical nonadiabatic dynamics protocol. Because the trajectories do not communicate with each other, a careful treatment needs to be made for the description of the nuclear coherences.

The surface hopping simulation protocol implemented in the SHARC37,38 program was employed to simulate the nonadiabatic photodissociation of thiophenol. Details of the protocol are given in ref 38. Herein, we provide a brief summary (see Supporting Information for computational details). The electronic structure calculations were performed using the MOLPRO39 program at the state-averaged CASSCF-(4/6)-6/31G\* level of theory with the four lowest adiabatic electronic states taken into account. The local diabatization algorithm based on the overlap matrices between the adiabatic electronic states \( \langle \psi_{\beta}(t) | \psi_{\alpha}(t + \Delta t) \rangle \) is used to propagate the electronic wave function under the effect of nonadiabatic couplings. We employed the energy-based decoherence correction scheme to describe the electronic decoherence when two surfaces drift away after passing the CI.40 The electronic population \( \rho_{\beta\beta} \) (diagonal element of the density matrix) and the coherence \( \rho_{\beta\alpha} \) (off-diagonal element of the density matrix) in the adiabatic electronic state can be calculated from the wave function coefficient vector \( c(t) \), \( \rho_{\beta\beta}(t) = |c(t)|^2 \) and \( \rho_{\beta\alpha}(t) = c(t)^*c(t) \). The Raman shift \( \Delta E_{ij} \) was obtained from the energy difference between the adiabatic electronic states \( S_i \) and \( S_j \). The transition charge density \( \sigma_{ij}(t) \) is calculated at every nuclear time step to account the geometrical change. All quantities presented in the paper are in the adiabatic electronic basis. The total propagation time was 49 fs, and the time steps for propagation of the nuclear and the electronic degrees of freedom were 0.05 and 0.002 fs, respectively. Forty-five initial geometries were sampled by using the quantum harmonic oscillator Wigner distribution around the ground state equilibrium geometry. The nonadiabatic surface hopping dynamics was initiated by promoting the system on \( S_i \) (\( \sigma^{\text{p}} \)) state. Forty-five trajectories were simulated and averaged out to provide the signals. Figures S2–4 shows the convergence of the population dynamics \( \rho_{ij} \) and coherences \( \rho_{12} \) and \( \rho_{01} \) with the number of trajectories taken into account.

We investigated the dynamics of the S–H dissociation of thiophenol that takes place after its initial photoexcitation in the \( S_2 \) (\( \sigma^{\text{p}} \)) state (impulsive excitation approximation; no external pump pulse was taken into account in the surface hopping dynamics). In practice, excitation at long wavelength \( \lambda > 275 \text{ nm} \) excites the system to the \( 1^1 \pi^* \) state, while the \( 1^1 \pi^* \) state can be excited at shorter excitation wavelengths.36,27,41 H-tunnelling from the \( 1^1 \pi^* \) state to the \( \sigma^{\text{p}} \) state may play a role in the photodissociation of thiophenol after an excitation to the \( S_1 \) (\( 1^1 \pi^* \)) state, which may not be properly described by the semiclassical surface hopping method. It is known that H-tunnelling plays an important role in a photodissociation of phenol after excitation to the \( S_1 \) (\( 1^1 \pi^* \)) state.42–44 Therefore, a photodissociation dynamics following an initial excitation to the \( S_1 \) (\( 1^1 \pi^* \)) state was considered in this paper.

Figure 2 shows the populations \( \rho_{ij} \) absolute value of coherences \( \rho_{ij} \), Raman shifts \( \Delta E_{ij} \), and the probability distribution of \( R_{S-H} \) vs time delay \( T \). The initially excited \( S_2 \) population at \( T = 0 \) relaxes to the ground state \( S_0 \) through the two conical intersections. As the excited state at the \( S_2 \) surface approaches the \( S_2/S_1 \) CI (CI-1), electronic coherence between \( S_2 \) and \( S_1 \) (\( \rho_{12} \)) builds up and peaks at 7 fs. At the same time, the \( S_2 \) population transfers to \( S_1 \) during \( T = 3–13 \) fs, i.e. \( \rho_{12} \) sharply decreases and \( \rho_{11} \) increases. A sharp drop of the energy gap between \( S_2 \) and \( S_1 \) (\( \Delta E_{12} \)) from 1.3 eV at \( T = 0 \) fs to \( T = 3–8 \) fs occurs, and the two electronic surfaces become degenerate. As the excited system through CI-1, \( \rho_{12} \) decreases, and \( \Delta E_{12} \) increases. Up to \( T = 13 \) fs, the S–H bond length \( R_{S-H} \) does not significantly vary as there is no major
change between the ground and the CI-1 geometries, merely a 0.2 Å change in S–H distance (as shown in Figure 2a).

The nonadiabatic dynamics between CI-1 to CI-2 involves a significant geometrical change associated with the S–H bond breaking. As the excited system approaches CI-1 at $T = 13\text{ fs}$, the electronic coherence $|\rho_{01}|$ and thus the ground state population $\rho_{00}$ start to grow. The energy gap $|\Delta E_{01}|$ then sharply drops from 6 eV to 0.

For better visualization of the distribution of the S–H distance in the course of the nonadiabatic dynamics, Figure 3 shows slices of Figure 2d and an overlay of corresponding geometries of 45 trajectories at selected time delays $T$. There is no significant geometrical rearrangement up to 5 fs. A noticeable S–H bond stretching starts at $T = 10\text{ fs}$. The nonadiabatic dynamics from CI-1 to CI-2 accompanies a significant deviation of the S–H bond distance from equilibrium.

After passing CI-2, the molecule may experience the S–H bond breaking (Figure 2d). Long-lived electronic coherence $|\rho_{01}|$ indicates that passing through CI-2 takes longer than CI-1. Some of the trajectories did not completely pass CI-2 in the 49 fs observation window of our simulation.

### SIGNATURES OF CONICAL INTERSECTIONS IN THE SXRI SIGNAL

Figure 4 shows the simulated SXRI signal for the nonadiabatic dynamics of thiophenol at several time delays $T$. The total signal $S_{\text{total}} = \sum_{i} S_{ij}$ and two dominant contributions $S_{12}$ and $S_{01}$ are shown to highlight the signal contributions at CI-1 and CI-2, where $S_{ij}$ is the signal contributed by $|i\rangle \langle j|$ coherence. $S_{12}$ ($S_{01}$) is a signature of $|1\rangle \langle 2| (|0\rangle \langle 1|)$ coherence at the CI-1 (CI-2). The top, middle, and bottom panels show $S_{12}$, $S_{01}$, and $S_{\text{total}}$, respectively. As shown in Figure 4, $S_{12}$ turns on at $T = 7\text{ fs}$ where the excited system reaches the CI-1, as evidenced by a large electronic coherence $|\rho_{12}|$ and small Raman shift $|\Delta E_{12}|$. As the excited system passed through CI-1 at $T = 7\text{ fs}$, $S_{12}$ fades away. $S_{01}$ is turned on at $T = 12.8\text{ fs}$ as the system reaches CI-2 where the ground and the first excited states cross. This is revealed by the fact that electronic coherence $|\rho_{01}|$ starts to grow, and the Raman shift $|\Delta E_{01}|$ becomes negligibly small at $T = 12.8\text{ fs}$. Therefore, the SXRI signal is a manifestation of the conical intersection.

Figure 5 depicts the product of off-diagonal density matrix element and the corresponding transition charge density $|\rho_{ij}| |\sigma_{ij}(r,t)|$ created by $|i\rangle \langle j|$ coherence, which is responsible for the SXRI signal $S_{ij}$ shown in Figure 4. The $|\rho_{12}(t)| |\sigma_{12}(r,t)|$ associated with CI-1 accounts for the electron transfer between a phenol and a S–H moiety while the $|\rho_{01}(t)| |\sigma_{01}(r,t)|$ associated with CI-2 accounts for mostly on site electron rearrangement at the sulfur atom. Clear distinction between the $|\rho_{ij}(t)| |\sigma_{ij}(r,t)|$ associated with conical intersections is revealed by the SXRI pattern. Figure 5 is created by using the real space transition charge density $\sigma_{ij}(r,T)$ and the density matrix element $\rho_{ij}(T)$, and $(\hat{\sigma}(r,T))$ can be reconstructed by three-dimensional inverse Fourier transform of $(\hat{\sigma}(r,T))$ obtained by deconvolution of the SXRI signal.

### CONCLUSIONS

We proposed a stimulated X-ray Raman imaging technique for probing nonadiabatic molecular dynamics. The technique
employs hard X-ray narrowband/broadband hybrid probe fields to generate a space-resolved image of a transition charge density which depends on the Raman frequency and the time delay $T$. SXRI provides information on the electronic transition at the level crossing region. Being a stimulated diffraction technique, the signal carries phase information, and the real-space image of the transition charge density can be reconstructed by its Fourier transform. More importantly, conical intersections can be distinguished by the diffraction patterns. Computationally, the simulation of SXRI signal requires use of the minimal-coupling Hamiltonian. This provides an intuitive picture and direct characterization on the electronic transition at the CI.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.9b03020.

1. Additional computational details; 2. derivation of the SXRI signal; 3. frequency-resolved SXRI signal; 4. convergence of the Raman frequency-$T$ absolute, real, and imaginary value of two dominant coherences, $\rho_{01}$ and $\rho_{12}$ according to number of trajectories accounted (PDF)

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**Notes**

The authors declare no competing financial interest.

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