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Direct Monitoring of Conical Intersection Passage Through Electronic Coherences in Twisted X-Ray Diffraction

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Abstract

Quantum coherences in electronic motions play a critical role in determining the pathways and outcomes of virtually all photophysical and photochemical molecular processes. However, the direct observation of electronic coherences in the vicinity of conical intersections (CIs) remains a formidable challenge. We propose a novel time-resolved twisted x-ray diffraction technique that can directly monitor the electronic coherences created as the molecule passes through the CI. We show that the contribution of electronic populations to this signal vanishes when using twisted x-ray beams, providing a direct measurement of transient electronic coherences in gas-phase molecules.

Main Text: The standard treatment of excited-state chemistry is based on the adiabatic separation of nuclear and electronic dynamics. Quantum chemistry then uses the Born-Oppenheimer approximation to compute adiabatic states. This widely used approximation breaks down when electronic and nuclear motions occur on a similar timescale and become strongly coupled. Conical intersections (CIs) are important examples where two or more adiabatic potential energy surfaces (PESs) become degenerate, resulting in strong non-adiabatic couplings between them. Because these regions allow for efficient, non-radiative electronic relaxations, they play critical roles in virtually all nonadiabatic reaction dynamics including photodissociation, isomerization, charge and energy transfer. Notable examples include the formation of vitamin D (1), photoinduced DNA damage (2), primary events in human vision (3) and charge transfer in organic photovoltaic devices (4). The conventional experimental signatures of CIs are indirect and based on electronic populations such as the fast conversion rates of electronic states or nuclear wave-packet bifurcation events (5, 6, 7, 8, 9). The direct experimental observation of transient electronic coherences generated as the molecule passes through a CI remains a formidable task as most contemporary ultrafast measurements are dominated by the signals from electronic populations which are significantly stronger than those from electronic coherences and are not specific to CIs.

In this theoretical study, we propose a novel ultrafast diffraction technique that can exclusively track electronic coherences at conical intersections with no contributions from electronic populations. In contrast to previously proposed stimulated ultrafast x-ray Raman technique that probes the energy profiles of electronic coherences (10), this technique directly images their spatial profiles through transient charge densities near a CI. As illustrated in panels 1a to 1c, we propose to use an optical pump laser to excite a gas-phase molecule (thiophenol) and probe its CI dynamics

by ultrafast non-resonant x-ray diffraction using twisted x-ray beams carrying orbital angular momentum (OAM, l). Rapid developments of both time-resolved gas-phase x-ray (11,12,13) and electron (14,15,8) diffraction techniques provide opportunities for tracking ultrafast structural changes, ‘molecular movies’, during chemical reactions with atomistic spatial and femtosecond temporal resolution. Theoretical studies have shown that standard ultrafast x-ray diffraction contains mixed elastic-inelastic coherence term originating from electronic coherences (16,17,18). During the passage through a CI, the mixed coherence term is found to be significantly (~ 4 orders of magnitude) weaker than the dominating elastic scattering contributions originated from electronic populations (19). Therefore, probing electronic coherences near a CI remains experimentally challenging for conventional (plane-wave) time-resolved diffraction.

Here, we show that this major problem can be solved by measuring the rotationally-averaged time-resolved x-ray diffraction signals of $S_l(q, T)$ and $S_{-l}(q, T)$, using twisted x-ray beams carrying positive (l) and negative OAM ($-l$). We find that when taking the difference of $S_l(q, T)$ and $S_{-l}(q, T)$, the contributions of electronic populations cancel out and only the desired electronic coherences survive. The proposed technique provides a direct measurement of the passage through CIs imprinted in the transient electronic coherences. Twisted beams, also known as vortex or OAM beams, possess a wavefront that twists along the beam propagation, independently of the beam polarization state. In this study we use linearly polarized Laguerre-Gaussian (LG) mode (20), which is a typical twisted light beam. Figure 1a shows an example of the spatial and phase profiles of a LG beam ($l = 1$) in the transvers plane. The OAM gives a twist to the phase that rotates along the propagation axis thereby forming a helical spatial wavefront. Various strategies have been developed to generate intense, hard-x-ray twisted beams at x-ray free-electron lasers (XFELs) (21,22,23), enabling ultrafast twisted x-ray diffraction of free molecules. Our proposed technique depends on twisted beams in an essential way and cannot be achieved with circular polarized light only carrying spin angular moment (SAM), as the SAM of light does not engage with the molecular charge density during the scattering process making it identical to x-ray diffraction of plane waves.

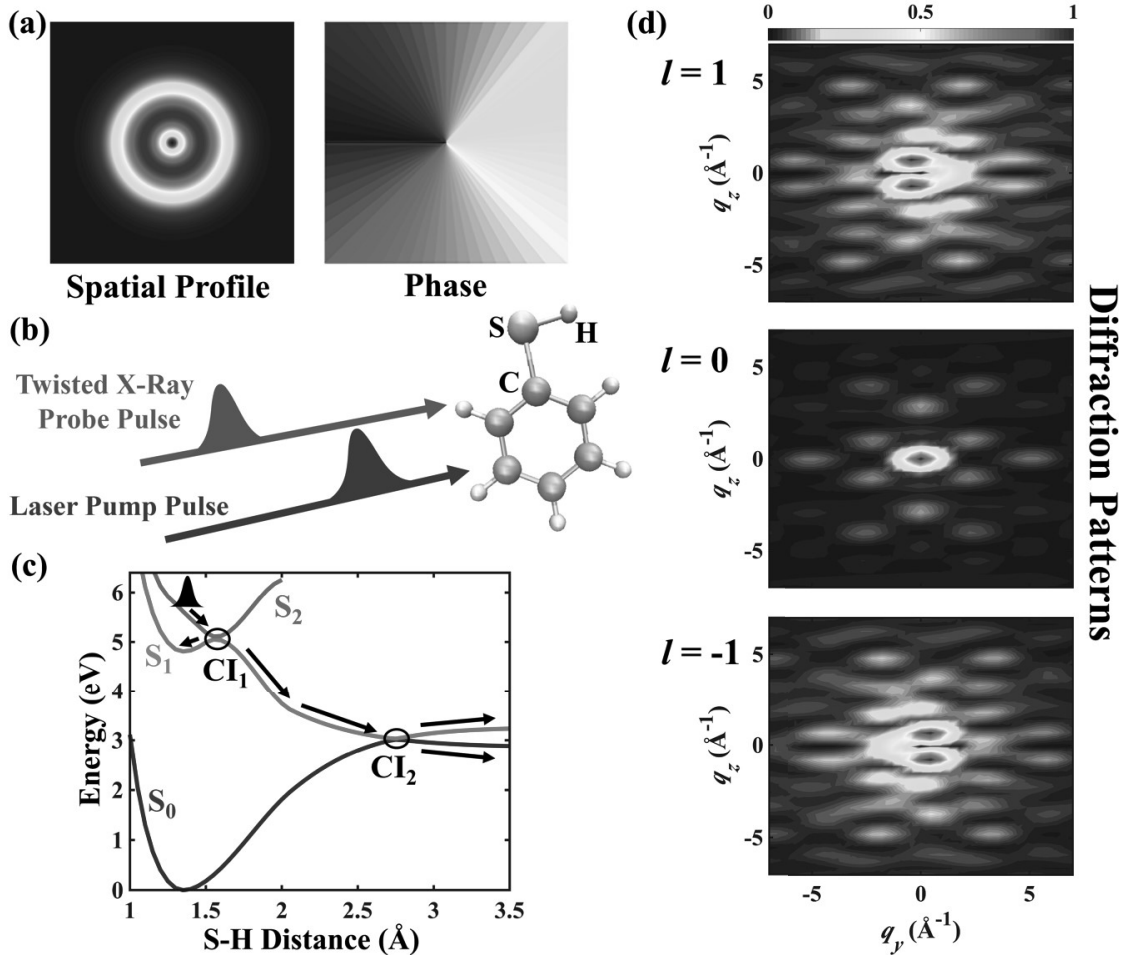


Figure 1. (a) Intensity (left) and phase (right) profile of the $l=1$ OAM light beam in the transverse plane. (b) The proposed experimental configuration. The photodissociation reaction of thiophenol is initiated by a laser pump pulse, and the resulting time-evolving molecular structure is probed by x-ray diffraction using twisted x-ray probe pulse with a variable time delay. (c) One-dimensional slice along the S-H distance of our two-dimensional potential energy surfaces for the S_2 , S_1 and S_0 adiabatic electronic states of thiophenol calculated at the SA4-CAS(12,11)/6-311++G(d,p) level of theory. Two conical intersections (CI_1 : S_2/S_1 and CI_2 : S_1/S_0) are marked with open circles. Black arrows sketch the reaction pathway of the nuclear wavepacket initially prepared in S_2 . (d) Two-dimensional diffraction patterns of ground-state thiophenol before pump excitation ($\tilde{S}_l^{\text{off}}(\mathbf{q})$) when using x-ray probe pulse with $l=1$ (top), $l=0$ (middle) and $l=-1$ (bottom) OAM, respectively. The signals are shown in the q_y - q_z plane ($q_x=0$) for an oriented molecule where its benzene ring is located in the y - z plane.

A molecular system driven by an optical laser can be described by the total time-dependent molecular many-body wavefunction which can be expanded in the adiabatic basis

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_k c_k(t) \chi_k(\mathbf{R}, t) \varphi_k(\mathbf{r}, \mathbf{R}) \quad (1)$$

where k labels the adiabatic electronic states, $\chi_k(\mathbf{R}, t)$ is the normalized nuclear wavepacket in the adiabatic electronic state $\varphi_k(\mathbf{r}, \mathbf{R})$, \mathbf{r} and \mathbf{R} are the electronic and nuclear coordinates, and $c_k(t)$

is the electronic state amplitude. Using Eq. 1, the time-evolving molecular charge density in real space is given by

$$\begin{aligned}\langle\sigma(\mathbf{r}, t)\rangle &= \sum_k \rho_{kk}(t) \langle\chi_k|\hat{\sigma}_{kk}(\mathbf{r})|\chi_k\rangle + 2\Re[\sum_{j>k} \rho_{jk}(t) \langle\chi_k|\hat{\sigma}_{kj}(\mathbf{r})|\chi_j\rangle] \\ &= \sigma_{\text{pop}}(\mathbf{r}, t) + \sigma_{\text{coh}}(\mathbf{r}, t)\end{aligned}\quad (2)$$

Here $\hat{\sigma}(\mathbf{r})$ is the electronic charge-density operator, $\rho_{kk}(t) = c_k^*(t)c_k(t)$ are real numbers representing the electronic populations at time t while the coherence terms, $\rho_{jk}(t) = c_k^*(t)c_j(t)$ with $j \neq k$, consists of complex numbers. The effective electronic coherence, $\rho_{jk}(t) \langle\chi_k|\chi_j\rangle$, is obtained from the combined electronic-nuclear wavefunction as the overlap of the nuclear wave packets. The total electronic charge density contains contributions from both time-evolving electronic population density $\sigma_{\text{pop}}(\mathbf{r}, t)$ and coherence density $\sigma_{\text{coh}}(\mathbf{r}, t)$. Upon transition to an excited electronic state, the effective electronic coherence of the system gradually builds up as the wavepacket passes the CI region where the nonadiabatic coupling is strong (24). Probing the time evolution of this electronic coherence thus provides direct evidence for the presence of the CI and offers a convenient way for monitoring CI dynamics.

The theoretical description of the time-resolved twisted x-ray diffraction (XRD) signal $\tilde{S}_l(\mathbf{q}, T)$ is based on the off-resonant single-molecule (gas-phase) time-resolved XRD in the minimal coupling picture (17,25). Similar to Eq. 2, the time-resolved twisted XRD signal $\tilde{S}_l(\mathbf{q}, T)$ can be partitioned into the sum of contributions from electronic populations $\tilde{S}_l^{\text{pop}}(\mathbf{q}, T)$ and coherences $\tilde{S}_l^{\text{coh}}(\mathbf{q}, T)$ (see details in SI),

$$\tilde{S}_l(\mathbf{q}, T) = \tilde{S}_l^{\text{pop}}(\mathbf{q}, T) + \tilde{S}_l^{\text{coh}}(\mathbf{q}, T) \quad (3)$$

where \mathbf{q} is the momentum transfer vector and T is the central time of x-ray probe pulse with respect to the pump. It is well known that the scattering of plane-wave photons results in centrosymmetric diffraction patterns, $S_0(\mathbf{q}) = S_0(-\mathbf{q})$, as stated by Friedel's law, which however does not hold for twisted beams (26). As illustrated in Figure 1d, diffraction patterns of x-ray beams carrying OAM ($l = \pm 1$ patterns) for an oriented molecule are no longer centrosymmetric, unlike the standard x-ray ($l = 0$) diffraction pattern. In addition, it has been demonstrated for static objects like apertures or crystals that x-ray diffraction patterns of twisted beams with opposite OAM (l) are linked by an inversion operation $S_l(\mathbf{q}) = S_{-l}(-\mathbf{q})$ (26). Turning to time-resolved diffraction from molecules, we find that this inversion relation still holds for the population contribution \tilde{S}_l^{pop} , i.e. $\tilde{S}_l^{\text{pop}}(\mathbf{q}, T) = \tilde{S}_{-l}^{\text{pop}}(-\mathbf{q}, T)$, but not for the coherence contribution $\tilde{S}_l^{\text{coh}}(\mathbf{q}, T)$ due to its mixed elastic-inelastic character and the presence of the complex electronic coherence terms ρ_{jk} (see SI for derivation). A ground-state molecule only has a population contribution thus its $l = 1$ pattern is rotated by π rad with respect to the $l = -1$ as shown in Figure 1d.

We next investigate the rotationally-averaged difference signal of gas-phase molecules

$$\Delta S_l(q, T) = \langle\tilde{S}_l(\mathbf{q}, T)\rangle_q - \langle\tilde{S}_{-l}(\mathbf{q}, T)\rangle_q = \Delta S_l^{\text{pop}}(q, T) + \Delta S_l^{\text{coh}}(q, T) \quad (4)$$

where q is the modulus of \mathbf{q} and $\langle\ldots\rangle_q$ denotes the rotationally-averaged diffraction signal. One can immediately see that $\Delta S_l^{\text{pop}}(q, T) = \langle\tilde{S}_l^{\text{pop}}(\mathbf{q}, T)\rangle_q - \langle\tilde{S}_{-l}^{\text{pop}}(\mathbf{q}, T)\rangle_q = 0$ from the centrosymmetric relation $\tilde{S}_l^{\text{pop}}(\mathbf{q}, T) = \tilde{S}_{-l}^{\text{pop}}(-\mathbf{q}, T)$, which implies a vanishing population contribution $\Delta S_l^{\text{pop}}(q, T) = 0$. Because the coherence term is not centrosymmetric ($\tilde{S}_l^{\text{coh}}(\mathbf{q}, T) \neq \tilde{S}_{-l}^{\text{coh}}(-\mathbf{q}, T)$), we obtain a purely electronic coherence signal $\Delta S_l(q, T) = \Delta S_l^{\text{coh}}(q, T)$ with no contributions from electronic population. $\Delta S_l(q, T)$ is constructed by elements of the effective

electronic coherence terms and the momentum-space electronic charge-density operators which carry OAM, $\hat{\sigma}_l(\mathbf{q})$. $\Delta S_l(q, T)$ is derived in SI.

We demonstrate the power of the proposed technique by applying it to a realistic and accessible molecular system (thiophenol photodissociation involving two CIs) calculated by exact quantum dynamical simulations. The corresponding Hamiltonian based on fully ab-initio quantum chemical simulations was introduced previously (27). Two CIs, S_2/S_1 and S_1/S_0 , were identified along the S-H dissociation channels in the course of the nonadiabatic relaxation process (28,29). In addition to S-H stretching, the in-plane S-H bending mode is known to be active in the conical intersection dynamics (30). Quantum dynamical simulations were performed by numerically solving the time-dependent Schrödinger equation for nuclei on the adiabatic potential energy surfaces of these two reactive coordinates (S-H distance and H-S-C angle), allowing for a fully quantum mechanical treatment of both electrons and nuclei, and including non-adiabatic couplings at the conical intersections. Since only two nuclear degrees of freedom contribute to the branching space of a conical intersection while the energy along all other degrees of freedom stays degenerate, quantum dynamical simulations of two reactive coordinates are commonly used to describe nonadiabatic dynamics involving conical intersections (31,32,33,34,35). For the ultrafast thiophenol S-H dissociation, the nuclear wavepacket is coherently funneled into a small reactive degrees of freedom, which exhibit by far the largest energy gradients that are captured in our Hamiltonian, as there is no time for many nuclear space degrees of freedom to be explored in sub-40 fs timescale considered in this study. The resulting dynamical pathways are marked by black arrows in Figure 1c. Upon excitation to S_2 , the wavepacket first reaches the S_2/S_1 CI within 10 fs and then bifurcates into two pathways. One portion of the nuclear wavepacket travels to the Franck-Condon region and localized on the S_1 surface, while the other part continues to pass the S_1/S_0 CI leading to hydrogen dissociation within 40 fs. We note that for much longer timescales (> 40 fs) our Hamiltonian could lose validity due to internal vibrational relaxation to other nuclear degrees of freedom and dissipation effects. Using a two-dimensional model Hamiltonian could then lead to a drastic overestimate of the electronic coherence.

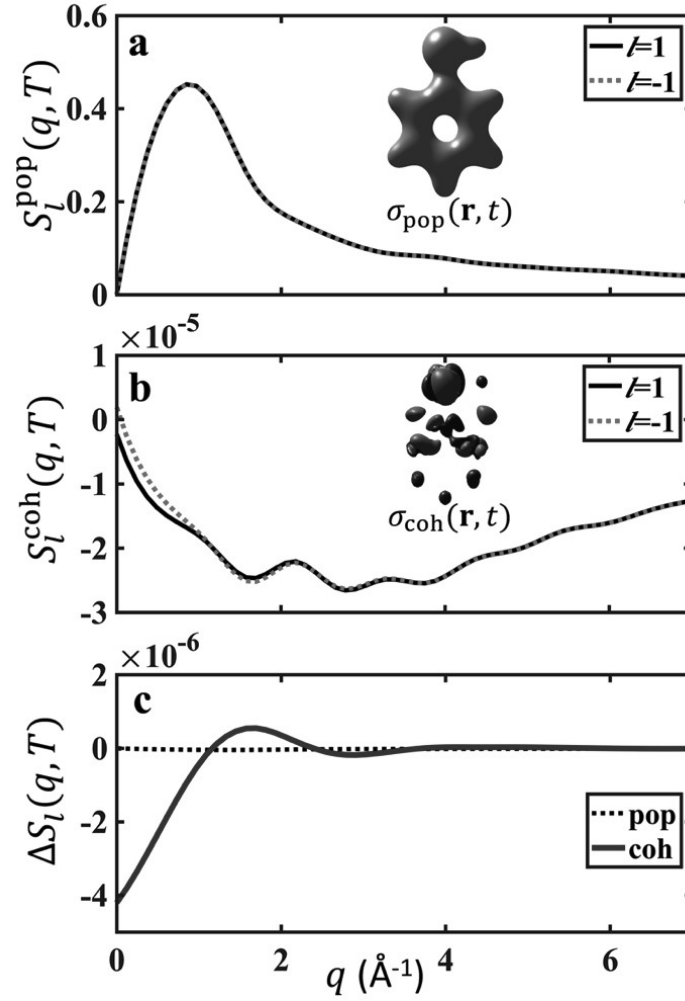


Figure 2. Rotationally-averaged diffraction signal at $T = 5.3$ fs after excitation. Population contribution $\tilde{S}_{l=\pm 1}^{\text{pop}}$ (top), coherence contribution $\tilde{S}_{l=\pm 1}^{\text{coh}}$ (middle) and difference signal $\Delta S_{l=1}^{\text{pop/coh}} = \tilde{S}_{l=1}^{\text{pop/coh}} - \tilde{S}_{l=-1}^{\text{pop/coh}}$ (bottom). Inserts: Isosurface plots of time-evolving population σ_{pop} (top) and coherent σ_{coh} (middle) charge densities in real space at $t = 5.3$ fs.

We have used the total molecular wavefunction of thiophenol to simulate the time-resolved rotationally-averaged diffraction signals, $\tilde{S}_{l=1}(q, T)$ for $l = 1$ and $l = -1$ OAM x-ray beams. Figure 2a and Figure 2b show the simulated results for both population contributions, $\tilde{S}_{l=\pm 1}^{\text{pop}}$, and coherence contributions, $\tilde{S}_{l=\pm 1}^{\text{coh}}$ at 5.3 fs time delay. It is clear that the population contribution to the time-resolved signal is identical for $l = 1$ and $l = -1$ OAM light, while their coherence contributions are distinct. Figure 2c demonstrates that the population contribution to the isotropic difference signal $\Delta S_l^{\text{pop}}(q, T)$ vanishes so that $\Delta S_l(q, T) = \Delta S_l^{\text{coh}}(q, T)$. We note that both population and coherence contributions appear mainly at small q values, because the time-evolving population and coherent charge densities are both diffuse and spread across the entire molecule in real space as illustrated in Figure 2 inserts. The diffraction signals at small q values (down to 0.3 \AA^{-1}) could be accessed by setting the main x-ray beam off-center from the hole of the detector similar to a recent ultrafast gas-phase electron diffraction setup (36).

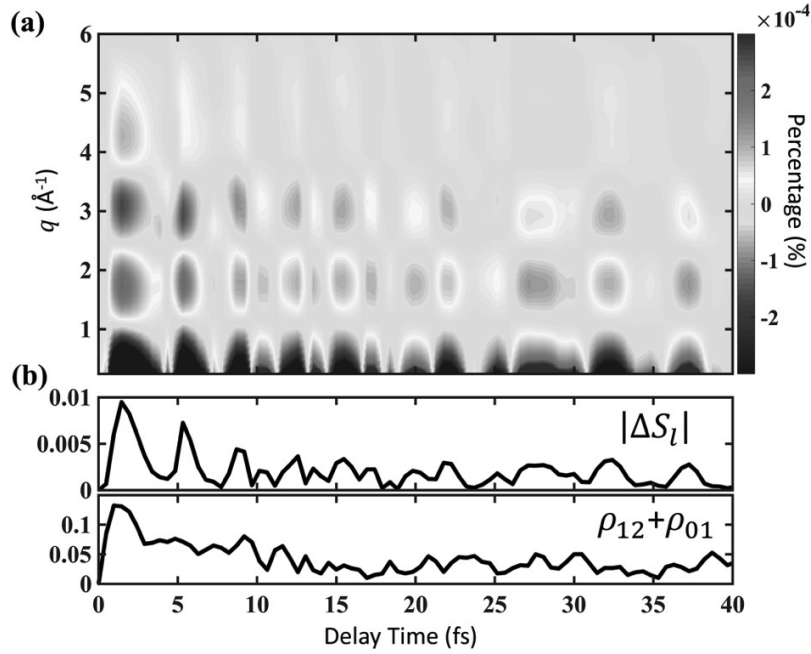


Figure 3. (a) Rotationally-averaged time-resolved difference signals, $\Delta S_{l=1}(q, T)$, in eq. 4. The signals are shown as percentages, $100 \frac{\Delta S_{l=1}(q, T)}{S_{l=1}^{\text{off}}(q)}$, where $S_{l=1}^{\text{off}}(q)$ is the reference x-ray diffraction signal before time zero. (b) Absolute value of the difference signal in (a) integrated over q (top) and the total coherence magnitude of the S_2/S_1 and S_1/S_0 electronic coherences calculated by quantum dynamics (bottom).

Figure 3 depicts the total time-resolved difference signal, which originates from the time-evolving coherent charge density, σ_{coh} in Eq. 2. The time dependence of the total signal comes from the time-evolving electronic coherence terms, and its variation with q reflects the real-space distribution of the coherent charge density, revealing both temporal and spatial profiles. Since electronic coherences are only generated when the nuclear wavepacket passes through the S_2/S_1 and S_1/S_0 CI, the overall signal in Figure 3a results from electronic coherences at both CIs. To investigate the temporal variations of the signal in Figure 3a, we show the time-dependent absolute difference signal integrated over q in the top panel of Figure 3b. For comparison, the sum of the S_2/S_1 and S_1/S_0 electronic coherence magnitudes obtained directly from the quantum dynamical simulations is shown in the bottom panel of Figure 3b. The integrated difference signal closely resembles the time-dependent electronic coherences in the molecule. The sharp rise of the signal after time zero indicates that the system starts to pass the first S_2/S_1 CI shortly after the laser excitation. The signal decreases within 10 fs, indicating that the wavepacket has reached the S_2/S_1 CI. The subsequent weak but finite signal up to 40 fs receives contributions from two electronic coherences: the S_2/S_1 electronic coherence generated near the Frank-Condon region when one portion of the wavepacket is localized in S_1 after bifurcation, and the S_1/S_0 electronic coherence generated when the other portion of the wavepacket passes the S_1/S_0 CI.

To further trace the origins of the signal in Figure 3, we have separated out the signal contributed by the S_1/S_0 electronic coherence. Figure 4a clearly shows different features compared to Figure 3a with different oscillation periods, demonstrating the electronic coherences generated at different CIs. We find that the signal in Figure 4 is about two orders of magnitude smaller than the total

signal shown in Figure 3. This is because the S_1/S_0 electronic coherence is much weaker than S_2/S_1 ($|\rho_{01}| \ll |\rho_{12}|$) as shown in Figures 3b and 4b. The S_1/S_0 electronic coherence is barely observable in the total signal. This is an intrinsic property of the specific system, rather than of the proposed setup. To make it detectable, one could use a different pumping strategy such as an infrared field resonant with the electronic transition in the S_1/S_0 CI region to noninvasively amplify the S_1/S_0 coherence (37). Similar to Figure 3b, the difference signal integrated over q shown in Figure 4b nicely monitors the time-dependence of the electronic coherence ρ_{01} . The proposed setup could thus provide a direct measurement of the distinct electronic coherences generated at different CIs, potentially allowing for their experimental separation. This would open a novel window into competing quantum pathways during ultrafast reactive molecular processes.

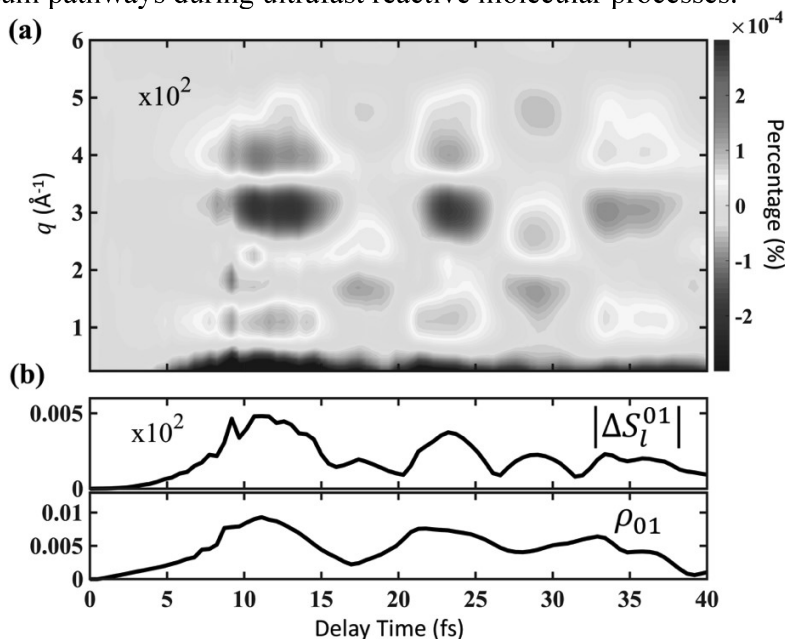


Figure 4. Same as Figure 3 but only for the S_1/S_0 electronic coherence.

In summary, we have demonstrated a novel technique for the direct monitoring of transient electronic coherences along the passage through CIs. Diffraction signals of gas-phase molecules are measured using twisted OAM carrying x-ray beams, which is suitable for concurrent ultrafast gas-phase XRD setup (38) by including an additional optical element on the incoming x-ray beam. We have used x-ray beams with $l = \pm 1$ OAM to demonstrate that the rotationally-averaged difference signal can directly monitor the time evolution of electronic coherences in a photoexcited molecule. The concept is also applicable to twisted x-ray beams with other nonzero numbers of l . The momentum profile of measurements with multiple l s could provide opportunities for reconstructing the complete time-evolving coherent charge density σ_{coh} in real space, where the concrete details and generality are subject to future studies. Moreover, because the nuclear wavepacket travels away from the Franck-Condon region rapidly after photoexcitation due to fast S-H dissociation, the initial coherence between S_2 and S_0 in the Franck-Condon region is ignored in this study. However, this initial coherence could persist and contribute fruitfully to the coherence signals in other dynamical processes which is worth further investigations. The direct imaging of electronic coherences in molecules opens brand new avenues for monitoring photophysical and photochemical processes, providing further opportunities for electronic coherent control over conical-intersection dynamics (39). Since the proposed technique is only

sensitive to the electronic coherences but not populations, it paves the way for the direct imaging of many other fundamental coherence phenomena in molecules; for example, tracking attosecond coherent electron motions in real space and time with state of the art attosecond XFELs (40,41).

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Competing interests

Authors declare that they have no competing interests.

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