

Novel Ultrafast Molecular Imaging Based on the Combination of X-ray and Electron Diffraction

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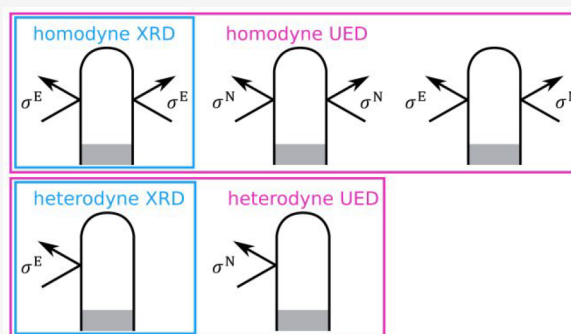
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ABSTRACT: Recent development of X-ray free-electron lasers and megaelectronvolt radio-frequency electron guns have made ultrafast X-ray and electron diffraction measurements possible, thereby capturing chemical dynamics with atomic-spatial and femtosecond-temporal resolutions. We present a unified formulation of standard homodyne-detected and heterodyne-detected signals for both techniques. Noting that X-rays scatter from molecular electrons while electrons scatter from both molecular electrons and nuclei, we show how the two diffraction signals can be combined to reveal novel chemical information that is unavailable by solely using each technique alone. By subtracting the homodyne-detected X-ray and electron diffraction signals, a mixed electronic–nuclear interference in electron diffraction can be identified with a self-heterodyne nature for the direct imaging of attosecond electron dynamics where the scattering off molecular nuclei serves as a local oscillator for the scattering off molecular electrons. By subtracting heterodyne-detected X-ray and electron diffraction, the purely nuclear charge density can be singled out.



1. INTRODUCTION

Time-resolved X-ray diffraction and electron diffraction are complementary real-space imaging techniques of ultrafast chemical dynamics in molecules.^{1–6} It is well-known that X-ray diffraction probes the electronic charge density whereas electron diffraction measures the total (electronic + nuclear) charge density. Because standard time-resolved gas-phase (single-molecule) diffraction uses homodyne detection, which gives the expectation values of products of charge density operators $\langle \hat{\sigma}^\dagger \hat{\sigma} \rangle$,⁷ reconstructing its signal requires the entire charge-density matrix, which goes beyond the expectation value of the charge density alone $\langle \hat{\sigma} \rangle$. Thus, the molecular charge density cannot be directly retrieved from homodyne-detected X-ray/electron diffraction signals. Heterodyne-detected diffraction, which requires an additional reference wave that interferes with the scattered wave, can solve the problem but at an additional experimental cost.⁸ Because heterodyne diffraction measures $\langle \hat{\sigma} \rangle$ while homodyne diffraction is related to $\langle \hat{\sigma}^\dagger \hat{\sigma} \rangle$, heterodyne signals are linear whereas homodyne signals are quadratic in the charge density. The time-evolving electronic charge density of the molecule in real space can thus be directly reconstructed from heterodyne-detected X-ray diffraction. Similarly, the time-evolving total (electronic + nuclear) charge density can be imaged by heterodyne-detected electron diffraction. It should be noted

that the purely nuclear charge density may not be detected by either heterodyne-detected X-ray or electron diffraction.

In this theoretical article, we show how ultrafast X-ray diffraction (XRD) and ultrafast electron diffraction (UED) signals may be combined to reveal novel information unavailable through either of them alone. We consider two types of combined X-ray and electron diffraction signals: (1) By subtracting *homodyne-detected* ultrafast X-ray and electron diffraction,⁹ a mixed electronic–nuclear interference in electron diffraction can be isolated for the direct imaging of attosecond electron dynamics in real space (Figure 1 top). (2) By subtracting *heterodyne-detected* ultrafast X-ray and electron diffraction,¹⁰ the purely nuclear charge density can be singled out, allowing the direct imaging of nuclear wavepacket dynamics (Figure 1, bottom).

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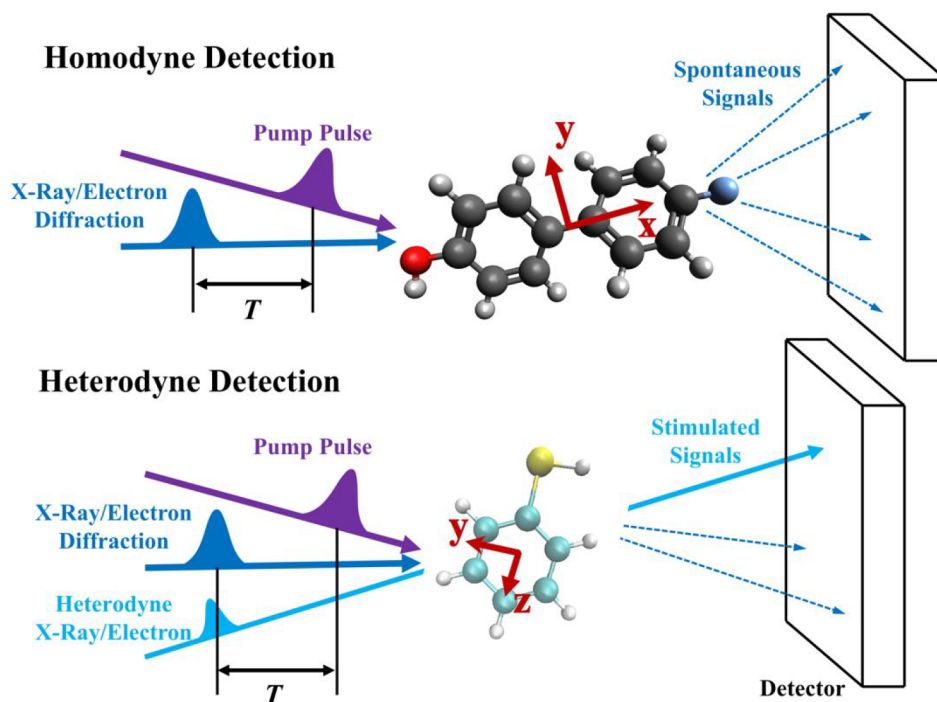


Figure 1. Top: Schematic of homodyne-detected X-ray/electron diffraction and the molecular structure of 4-fluoro-4'-hydroxybiphenyl. Bottom: Schematic of heterodyne-detected X-ray/electron diffraction and the molecular structure of thiophenol.

2. THEORY

2.1. Homodyne- vs Heterodyne-Detected Diffraction.

The time-dependent molecular many-electron wave function prepared by a pump pulse may be expanded as

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i c_i(t) \chi_i(\mathbf{R}, t) \varphi_i(\mathbf{r}, \mathbf{R}) \quad (1)$$

where i labels the adiabatic electronic states, $\chi_i(\mathbf{R}, t)$ is the normalized nuclear wavepacket in the adiabatic electronic state $\varphi_i(\mathbf{r}, \mathbf{R})$, $\mathbf{r}$ and $\mathbf{R}$ are the electronic and nuclear coordinates, t is time, and c_i is the electronic state amplitude.

The time-resolved single-molecule (gas-phase) homodyne diffraction signal is given by^{7,11}

$$S_{\text{hom}}(\mathbf{q}, T) \propto W_0(\Delta\omega) \int dt |\mathbf{A}_X(t - T)|^2 \tilde{S}_{\text{hom}}(\mathbf{q}, t) \quad (2)$$

where $\mathbf{A}_X(t - T)$ is the X-ray/electron probe pulse vector potential at delay time T from the pump pulse, $\mathbf{q}$ is the scattering momentum transfer, $W_0(\Delta\omega)$ is a window function for a frequency detection window $\Delta\omega$, and $\tilde{S}_{\text{hom}}(\mathbf{q}, t)$ is the time-dependent molecular response in homodyne diffraction. We assume a window function much broader than the relevant electronic transition energies of the system so that $W_0(\Delta\omega)$ is independent of the molecular response.^{9,12,13}

We note that homodyne signals constitute coherent spontaneous emission whereas heterodyne signals are generated by stimulated emission.¹⁴ The homodyne-detected diffraction signal in eq 2 thus measures the modulus square of an amplitude, so that it is not sensitive to the phase of the probe pulse. The phase information can be retrieved by using an additional X-ray/electron heterodyne pulse that interferes with the spontaneously emitted photons/electrons, which amounts to heterodyne (stimulated) detection.

The time-resolved heterodyne-detected diffraction signal is given by^{8,10}

$$S_{\text{het}}(\mathbf{q}, T) \propto 2\mathcal{I} \int dt \mathbf{A}_X(t - T) \mathbf{A}_{\text{het}}^*(t - T) \tilde{S}_{\text{het}}(\mathbf{q}, t) \quad (3)$$

where $\mathbf{A}_{\text{het}}^*(t - T)$ is the conjugate heterodyne reference X-ray/electron pulse and $\tilde{S}_{\text{het}}(\mathbf{q}, t)$ is the time-dependent molecular response in heterodyne diffraction. The experimental requirements for the heterodyne-detected diffraction signal have been discussed elsewhere.⁸ Briefly, it employs two coincident, noncollinear pulses with a controlled relative phase. The scattering wavevector $\mathbf{q}$ can be scanned by varying the angle between the probe $\mathbf{A}_X$ and the reference pulse $\mathbf{A}_{\text{het}}$.

The homodyne-detected X-ray diffraction, $\tilde{S}_{\text{hom}}(\mathbf{q}, t)$, in eq 2 is given by

$$\tilde{S}_{\text{hom}}^{\text{XRD}}(\mathbf{q}, t) = \sum_{ijk} \rho_{ji}(t) \langle \chi_i(t) | \hat{\sigma}_{ik}^E(-\mathbf{q}) \hat{\sigma}_{kj}^E(\mathbf{q}) | \chi_j(t) \rangle \quad (4)$$

where $\rho_{ji}(t) = c_i^*(t)c_j(t)$ and $\hat{\sigma}_{kj}^E(\mathbf{q})$ is the electronic charge-density operator in momentum space.

The heterodyne-detected X-ray diffraction, $\tilde{S}_{\text{het}}(\mathbf{q}, t)$, in eq 3 is given by

$$\tilde{S}_{\text{het}}^{\text{XRD}}(\mathbf{q}, t) = \sum_{ij} \rho_{ji}(t) \langle \chi_i(t) | \hat{\sigma}_{ij}^E(\mathbf{q}) | \chi_j(t) \rangle \quad (5)$$

where $\sigma_{\text{tot}}^E(\mathbf{q}, t) = \sum_{ij} \rho_{ji}(t) \langle \chi_i(t) | \hat{\sigma}_{ij}^E(\mathbf{q}) | \chi_j(t) \rangle$ is the time-evolving electronic charge density of the molecule in momentum space.

Unlike X-ray scattering that is dominated by the molecular electronic charge density, electron scattering is originated from the electrostatic Coulomb interaction of the incoming electrons with both molecular electrons and nuclei.¹⁵ In homodyne-detected electron diffraction, $\tilde{S}_{\text{hom}}(\mathbf{q}, t)$ in eq 2 is written as

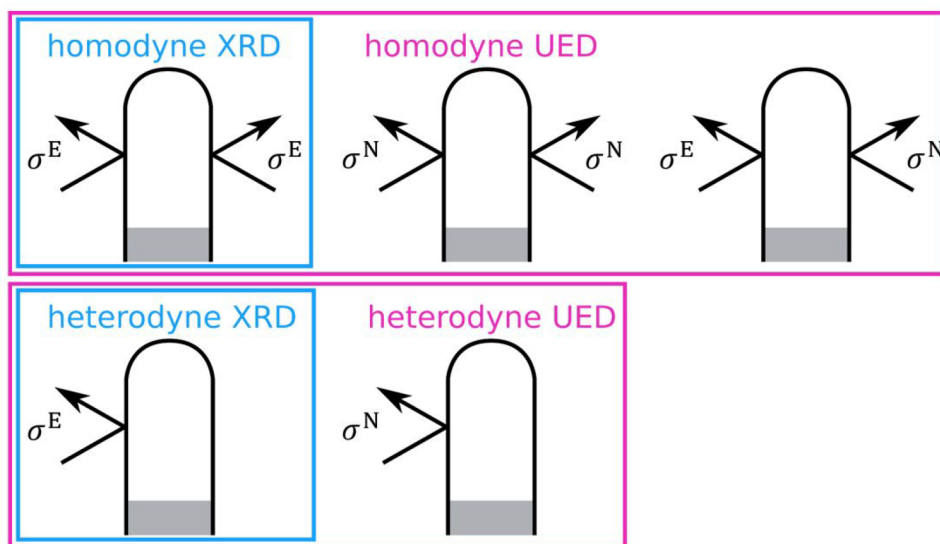


Figure 2. Top: Loop diagrams for single-molecule homodyne XRD (blue box) and UED (pink box). Bottom: Loop diagrams for single-molecule heterodyne XRD (blue box) and UED (pink box).

$$\begin{aligned}\tilde{S}_{\text{hom}}^{\text{UED}}(\mathbf{q}, t) &= \sum_{ijk} \rho_{ji}(t) \langle \chi_i(t) | \hat{\sigma}_{ik}^E(-\mathbf{q}) \hat{\sigma}_{kj}^E(\mathbf{q}) | \chi_j(t) \rangle \\ &+ \sum_i \rho_{ii}(t) \langle \chi_i(t) | \hat{\sigma}_{ii}^N(-\mathbf{q}) \hat{\sigma}_{ii}^N(\mathbf{q}) | \chi_i(t) \rangle \\ &+ 2\mathcal{R} \left[\sum_{ij} \rho_{ji}(t) \langle \chi_i(t) | \hat{\sigma}_{ij}^E(-\mathbf{q}) \hat{\sigma}_{jj}^N(\mathbf{q}) | \chi_j(t) \rangle \right] \\ &= \tilde{S}_{\text{hom}}^{\text{elec}}(\mathbf{q}, t) + \tilde{S}_{\text{hom}}^{\text{nucl}}(\mathbf{q}, t) + \tilde{S}_{\text{hom}}^{\text{mixed}}(\mathbf{q}, t)\end{aligned}\quad (6)$$

where $\hat{\sigma}_{ii}^N(\mathbf{q})$ is the nuclear charge-density operator in momentum space, $\tilde{S}_{\text{hom}}^{\text{elec}}(\mathbf{q}, t) = \tilde{S}_{\text{hom}}^{\text{XRD}}(\mathbf{q}, t)$ is the electronic contribution to the homodyne diffraction signal, $\tilde{S}_{\text{hom}}^{\text{nucl}}(\mathbf{q}, t)$ is the nuclear contribution to the signal, and $\tilde{S}_{\text{hom}}^{\text{mixed}}(\mathbf{q}, t)$ is the mixed electronic–nuclear interference in electron diffraction as can be read from the top panel of Figure 2.

Similarly, the heterodyne-detected electron diffraction, $\tilde{S}_{\text{het}}(\mathbf{q}, t)$, in eq 3 is given by

$$\begin{aligned}\tilde{S}_{\text{het}}^{\text{UED}}(\mathbf{q}, t) &= \sum_{ij} \rho_{ji}(t) \langle \chi_i(t) | \hat{\sigma}_{ij}^E(\mathbf{q}) | \chi_j(t) \rangle \\ &+ \sum_i \rho_{ii}(t) \langle \chi_i(t) | \hat{\sigma}_{ii}^N(\mathbf{q}) | \chi_i(t) \rangle \\ &= \tilde{S}_{\text{het}}^{\text{elec}}(\mathbf{q}, t) + \tilde{S}_{\text{het}}^{\text{nucl}}(\mathbf{q}, t)\end{aligned}\quad (7)$$

where $\sigma_{\text{tot}}^N(\mathbf{q}, t) = \sum_i \rho_{ii}(t) \langle \chi_i(t) | \hat{\sigma}_{ii}^N(\mathbf{q}) | \chi_i(t) \rangle$ is the time-evolving nuclear charge density of the molecule in momentum space. $\tilde{S}_{\text{het}}^{\text{elec}}(\mathbf{q}, t) = \tilde{S}_{\text{het}}^{\text{XRD}}(\mathbf{q}, t)$ is the electronic contribution to the heterodyne diffraction signal, and $\tilde{S}_{\text{het}}^{\text{nucl}}(\mathbf{q}, t)$ is the nuclear contribution to the heterodyne electron diffraction signal as can be read from the bottom panel of Figure 2.

3. RESULTS AND DISCUSSION

3.1. Imaging Attosecond Purely Electron Dynamics by Subtracting Homodyne Signals. Attosecond electron dynamics in molecules where the nuclei are static is known as charge migration and has been reported in recent experiments.^{16–21} Even though ultrafast homodyne-detected X-ray

scattering has been theoretically proposed to study charge migration,^{22–24} the molecular charge density in real space cannot be directly retrieved from such signals as it measures the expectation values of products of charge-density operators. Heterodyne-detected X-ray diffraction could achieve this in molecules,^{8,25} but its experimental realization is more complex. Below we discuss a novel technique for the real-space imaging of attosecond electron dynamics in isolated molecules based on combining ultrafast homodyne-detected X-ray and electron diffraction signals.⁹ This is achieved by isolating the mixed contribution, $\tilde{S}_{\text{hom}}^{\text{mixed}}(\mathbf{q}, t)$, in eq 6.

By subtracting the ultrafast homodyne-detected X-ray (eq 4) and electron diffraction (eq 6) signals with careful normalization, one obtains $S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t)$ as

$$\begin{aligned}S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t) &= \eta \tilde{S}_{\text{hom}}^{\text{UED}}(\mathbf{q}, t) - \tilde{S}_{\text{hom}}^{\text{XRD}}(\mathbf{q}, t) \\ &= \tilde{S}_{\text{hom}}^{\text{nucl}}(\mathbf{q}, t) + \tilde{S}_{\text{hom}}^{\text{mixed}}(\mathbf{q}, t)\end{aligned}\quad (8)$$

where η is a normalization factor accounting for the different X-ray and electron scattering cross sections.⁴ In the charge migration regime where nuclear motions can be neglected, $\tilde{S}_{\text{hom}}^{\text{nucl}}(\mathbf{q}, t)$ is independent of time t , and the time-dependent difference signal $\Delta S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t)$ is given by

$$\begin{aligned}\Delta S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t) &= S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t) - S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t < 0) \\ &= \Delta \tilde{S}_{\text{hom}}^{\text{mixed}}(\mathbf{q}, t) = 2\mathcal{R}[\Delta \sigma_{\text{tot}}^E(-\mathbf{q}, t) \sigma_0^N(\mathbf{q})]\end{aligned}\quad (9)$$

where $\Delta \sigma_{\text{tot}}^E(\mathbf{q}, t) = \sigma_{\text{tot}}^E(\mathbf{q}, t) - \sigma_0^E(\mathbf{q})$ is the difference electronic charge density in $\mathbf{q}$ -space. $\sigma_0^E(\mathbf{q})$ is the total electronic charge density prior to the pump pulse, i.e., $\sigma_{\text{tot}}^E(\mathbf{q}, t < 0) = \sigma_0^E(\mathbf{q})$. Equation 9 shows that the time-dependent difference signal $\Delta S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t)$ only comes from the mixed nuclear–electronic term $\Delta \tilde{S}_{\text{hom}}^{\text{mixed}}(\mathbf{q}, t)$. Because the molecular nuclei are frozen during the attosecond charge migration dynamics, the resulting time-dependent difference signal constitutes an interference between the time-evolving electronic charge density $\sigma_{\text{tot}}^E(\mathbf{q}, t)$ and the ground-state nuclear charge density $\sigma_0^N(\mathbf{q})$ which remains static and serves as a reference local oscillator. This generates a heterodyne signal without employing an additional field. $\Delta S_{\text{hom}}^{\text{diff}}(\mathbf{q}, t)$ thus can

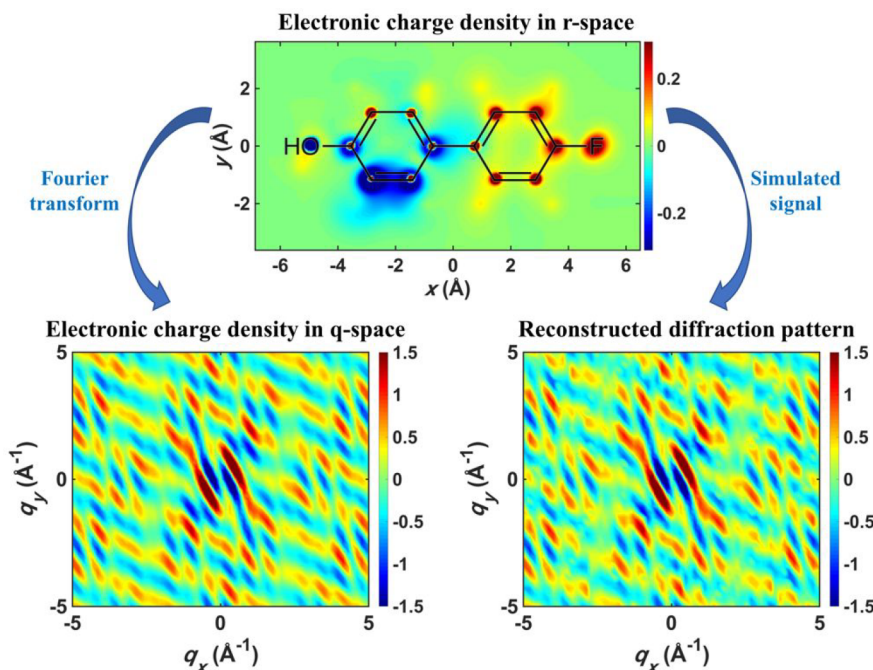


Figure 3. Top: Difference electronic charge density of 4-fluoro-4'-hydroxybiphenyl in real space $\Delta\sigma_{\text{tot}}^E(\mathbf{r}, t)$ after excitation with the X-ray pump pulse tuned to the oxygen K-edge. The molecular Lewis structure is overlaid with the color plot. An oriented molecule located in the x - y plane is assumed (see Figure 1 for the Cartesian coordinates). The charge density is displayed in the x - y plane by integrating over z . Bottom left: Real part of the Fourier-transformed difference electronic charge density $\mathcal{R}[\Delta\sigma_{\text{tot}}^E(\mathbf{q}, t)]$. Bottom right: Diffraction signal constructed by $\mathcal{R}\left[\frac{\Delta\sigma_{\text{tot}}^{\text{diff}}(\mathbf{q}, t)}{\sigma_0^N(\mathbf{q})}\right]$. Both the electronic charge density and the signal are displayed in the q_x - q_y plane ($q_z = 0$). The results from the oxygen excitation at 2.2 fs are used for demonstration. The full electron dynamics is discussed in ref 9.

directly measure the time-evolving electronic charge density, generating movies of charge migration dynamics in molecules. We note that although the $\sigma_0^N(\mathbf{q}, t)$ remains constant as a function of time t , it has a nontrivial distribution as a function of $\mathbf{q}$ determined by the nuclear geometry of the ground-state molecule. The ground-state nuclear geometry is assumed as a prior knowledge that can be obtained by either static diffraction measurements or high-level quantum chemistry calculations. The $\sigma_0^N(\mathbf{q})$ can then be calculated from the ground-state nuclear geometry using $\sigma_0^N(\mathbf{q}) = \sum_a Z_a e^{i\mathbf{q}\cdot\mathbf{R}_a}$, where a labels the a th atom with atomic number Z_a at position $\mathbf{R}_a$.

Figure 3 illustrates how $\Delta\sigma_{\text{tot}}^{\text{diff}}$ can be used to reconstruct the time-evolving electronic charge density. The attosecond electron dynamics of 4-fluoro-4'-hydroxybiphenyl prepared by a broadband soft X-ray excitation resonant with the oxygen K-edge was simulated by exactly solving the time-dependent Schrödinger equation for molecular electrons.⁹ The resonant X-ray excitation creates a localized negative density “hole” near the excited oxygen core region and a delocalized positive valence “electron” across the entire molecule. Figure 3 shows a snapshot of the electron dynamics at 2.2 fs. A weaker delocalized negative density hole around the right benzene ring also manifests in the real-space panel of Figure 3. This is due to the relaxation of occupied molecular orbitals after the generation of a 1s core hole upon excitation. This feature is well captured by the simulated $\Delta\sigma_{\text{tot}}^{\text{diff}}$ diffraction signal. The $\Delta\sigma_{\text{tot}}^{\text{diff}}$ signal originates from $\Delta\sigma_{\text{tot}}^E(\mathbf{q}, t)\sigma_0^N(\mathbf{q})$ rather than the time-evolving electronic charge density $\Delta\sigma_{\text{tot}}^E(\mathbf{q}, t)$. A protocol based on calculating $\sigma_0^N(\mathbf{q})$ from the ground-state nuclear geometry of the molecule is used to obtain the reconstructed

diffraction pattern in Figure 3. It is important to obtain an accurate ground-state nuclear geometry of the molecule as it could affect the accuracy of the reconstructed $\Delta\sigma_{\text{tot}}^E(\mathbf{q}, t)$. The resulting diffraction signal is nearly identical with the Fourier-transformed electronic charge density in $\mathbf{q}$ -space. This allows to invert the signal from momentum space to real space for generating a “molecular movie” of attosecond charge migration.

3.2. Imaging Femtosecond Purely Nuclear Charge Density by Subtracting Heterodyne Signals. Femtosecond optical pulses can generate a coherent superposition of many vibrational states and initiate photochemical reactions described by coherent nuclear wavepacket motions.^{26,27} However, the direct measurement of purely nuclear charge density in molecules with ultrafast spectroscopy remains challenging since the probe pulses usually measure the energy levels rather than the structure. The nuclear charge density has long been detected on the microsecond time scale by neutron scattering,^{28,29} which misses the much faster elementary chemical reaction events. We now introduce a novel technique that can directly image femtosecond purely nuclear charge density by combining the ultrafast heterodyne-detected X-ray and electron diffraction signals.¹⁰ This can be realized by isolating $\tilde{\sigma}_{\text{het}}^{\text{nuc}}(\mathbf{q}, t)$ in eq 7.

By subtracting the ultrafast heterodyne-detected X-ray (eq 5) and electron diffraction (eq 7) signals with a proper normalization, one obtains $\tilde{\sigma}_{\text{het}}^{\text{diff}}$ as

$$\tilde{\sigma}_{\text{het}}^{\text{diff}}(\mathbf{q}, t) = \eta' \tilde{\sigma}_{\text{het}}^{\text{UED}}(\mathbf{q}, t) - \tilde{\sigma}_{\text{het}}^{\text{XRD}}(\mathbf{q}, t) = \tilde{\sigma}_{\text{het}}^{\text{nuc}}(\mathbf{q}, t) \quad (10)$$

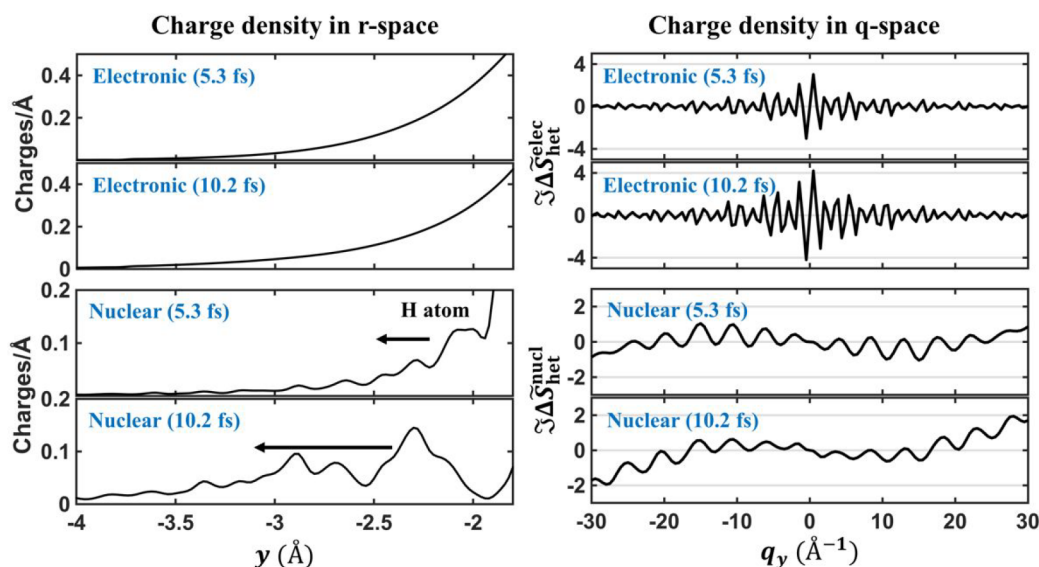


Figure 4. Left: Real-space electronic (top) and nuclear (bottom) charge densities of thiophenol along the y axis at selected delay times. The charge densities are integrated over the x and the z axis for $z < -1$ Å. The molecule is located in the y - z plane (see Figure 1 for the Cartesian coordinates). Right: Simulated time-resolved difference diffraction signals from for electronic ($\Delta S_{\text{het}}^{\text{elec}}(q, t)$, top) and nuclear charge densities ($\Delta S_{\text{het}}^{\text{nucl}}(q, t)$, bottom), respectively. The signals are shown along q_y and ($q_x = q_z = 0$). The full dynamics is discussed in ref 10.

where η' is a normalization factor.¹⁰ The time-dependent difference signal $\Delta S_{\text{het}}^{\text{diff}}$ is then given by

$$\begin{aligned} \Delta S_{\text{het}}^{\text{diff}}(\mathbf{q}, t) &= S_{\text{het}}^{\text{diff}}(\mathbf{q}, t) - S_{\text{het}}^{\text{diff}}(\mathbf{q}, t < 0) = \Delta \tilde{S}_{\text{het}}^{\text{nucl}}(\mathbf{q}, t) \\ &= \Delta \sigma_{\text{tot}}^{\text{N}}(\mathbf{q}, t) \end{aligned} \quad (11)$$

where $\Delta \sigma_{\text{tot}}^{\text{N}}(\mathbf{q}, t) = \sigma_{\text{tot}}^{\text{N}}(\mathbf{q}, t) - \sigma_0^{\text{N}}(\mathbf{q})$ is the difference nuclear charge density in $\mathbf{q}$ -space. $\sigma_0^{\text{N}}(\mathbf{q})$ is the nuclear charge density prior to the pump pulse, i.e., $\sigma_{\text{tot}}^{\text{N}}(\mathbf{q}, t < 0) = \sigma_0^{\text{N}}(\mathbf{q})$. Thus, the time-dependent difference signal $\Delta S_{\text{het}}^{\text{diff}}$ directly and exclusively probes the time-evolving nuclear charge density in real space.

Figure 4 illustrates how $\Delta S_{\text{het}}^{\text{diff}}$ can be applied toward imaging the purely nuclear charge density. The nuclear wavepacket dynamics of the photodissociation of the S–H bond in thiophenol was calculated by exact quantum dynamical simulations. The Hamiltonian based on fully ab initio quantum chemical simulations was introduced previously.¹⁰ Quantum dynamical simulations were performed by numerically solving the time-dependent Schrödinger equation for nuclei on the adiabatic potential energy surfaces of the two reactive coordinates (S–H stretching and in-plane S–H bending), allowing for a fully quantum mechanical treatment of both electrons and nuclei. Figure 4 shows the resulting time-evolving electronic (top panel) and nuclear (bottom panel) charge density in both real and momentum space. It is clear that the nuclear wavepacket dynamics is better resolved in the nuclear signals, $\Delta S_{\text{het}}^{\text{nucl}}$, as the nuclear charge densities are unmasked by the surrounding much more delocalized electron densities. The time-dependent difference signal $\Delta S_{\text{het}}^{\text{diff}}$ can thus directly image the nuclear wavepacket motion of the hydrogen atom during the S–H bond breaking as illustrated in the bottom two panels of the Figure 4.

4. CONCLUSIONS

We have simulated the homodyne and heterodyne-detected time-resolved X-ray and electron diffraction signals. We find that novel chemical information can be revealed by combining the two signals, which is not possible by using either signal

alone. We showed that attosecond electron dynamics can be directly imaged by combined homodyne-detected ultrafast X-ray and electron diffraction. This is achieved by singling out the mixed electronic–nuclear interference term in homodyne-detected electron diffraction resulting in a self-heterodyne detection of the electronic charge density. We further showed that the purely nuclear charge density during a nuclear wavepacket dynamics can be imaged by combining heterodyne-detected ultrafast X-ray and electron diffraction signals. Careful normalization (i.e., η and η') of the signal for both measurements is crucial for the proper subtraction of X-ray and electron diffraction signals in order to isolate the desired signal. Experimental conditions such as the different scattering cross sections, scattering backgrounds, and detector responses for X-rays and electrons need to be treated properly. Moreover, the diffraction signals should be deconvoluted with their respective instrument functions before subtraction to account for the potential temporal difference of the X-ray and electron pulse envelopes.

The proposed measurements are very challenging: attosecond temporal resolution is required for both homodyne X-ray and electron diffraction to probe charge migration. This could become feasible in the near future with the development of XFELs^{30,31} and relativistic megaelectronvolt electron beams.^{32,33} Heterodyne detection is needed for both X-ray and electron diffraction to image purely nuclear charge density. This has been implemented in the field of holographic imaging^{34–36} but has not been extended yet to the ultrafast imaging of molecular dynamics. The required experimental effort is warranted as it can reveal chemical information unavailable otherwise.

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Notes

The authors declare no competing financial interest.

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