

# Attosecond momentum-resolved resonant inelastic x-ray scattering for imaging coupled electron-hole dynamics

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Improving our understanding of electron dynamics is essential for advancing energy transfer, optoelectronics, light harvesting systems and quantum computing. Recent developments in attosecond x-ray sources provide the fundamental possibility of observing these dynamics with atomic-scale resolution. However, connecting a time-resolved signal to dynamics is challenging due to the broad bandwidth of an attosecond probe pulse. This makes exploring the capabilities of different attosecond imaging techniques crucial. Here, we propose attosecond momentum-resolved resonant inelastic x-ray scattering as a prominent technique for tracking ultrafast dynamics. We demonstrate that the scattering signal contains an information about the instantaneous distribution of charge density across the scattering atoms. To illustrate this, we consider scattering from an  $\alpha$ -sexithiophene molecule, in which coupled electron-hole dynamics are excited.

The absorption of an optical or an ultraviolet photon can lead to the neutral excitation of a molecule driving the motion of a charge density [1]. This motion plays a crucial role in energy transfer [2], optoelectronics [3–5], photoelectrochemical sensing [6–10], quantum computing [11–15], and for light-harvesting systems [16, 17]. The time scales of electron dynamics range from sub- to few femtoseconds, and the relevant spatial scales are interatomic distances ranging from Ångstrom to nanometers. The direct observation of electron dynamics requires a combination of attosecond temporal and atomic spatial resolution [18, 19].

Attosecond pump-probe spectroscopy has matured over the past two decades providing the temporal resolution necessary to observe electron dynamics using spectroscopy techniques [20–25]. Attosecond imaging requires going beyond spectroscopy and the application of scattering and diffraction techniques, which has recently become possible at free-electron laser sources [26–30]. Attosecond imaging using a pump-probe scheme remains challenging, but efforts are being made to improve the control and stability of attosecond x-ray experiments [31–33]. Attosecond imaging poses an additional challenge in interpreting signals due to the broad bandwidth of attosecond pulses and the interaction of light with non-stationary electron states. In order to guide experimental developments, it is necessary to investigate and propose beneficial schemes for imaging electronic motion using broad-bandwidth pulses.

X-ray scattering (XRS) with hard x rays provides (sub-)nanometer spatial resolution. This process is governed by two terms of the light-matter interaction Hamiltonian, namely,  $\mathbf{A} \cdot \mathbf{p}$  and  $\mathbf{A}^2$ , where  $\mathbf{A}$  is the vector potential of an x-ray field and  $\mathbf{p}$  is the momentum operator [34]. If an x-ray pulse is resonant with the core excitation energy of a system, the former term dominates, and x-ray scattering is referred to as resonant [35]. If the x-ray pulse is detuned from any transition, the latter term

dominates, and scattering is referred to as non-resonant. Non-resonant XRS [36–38] and sum frequency diffraction [39] have been proposed to follow valence-electron motion, attosecond ring currents [40], and conical intersection dynamics [41]. Hybrid x-ray/electron diffraction schemes have also been suggested to trace coupled electron-nuclear dynamics [42, 43].

The advantage of ultrafast resonant x-ray scattering over non-resonant XRS for attosecond imaging is that it enables the selective enhancement of the scattering contribution from the (quasi)particles involved in the dynamics [44, 45]. The conventional resonant x-ray scattering technique measures the momentum of elastically scattered photons [35], while resonant inelastic x-ray scattering (RIXS) is a spectroscopic technique [46]. Momentum-resolved RIXS combines the strengths of both techniques. Several theoretical works have been developed to describe RIXS [47–49] and momentum-resolved RIXS [44, 45, 50, 51] from non-stationary electron systems. It has been demonstrated that an attosecond momentum-resolved resonant x-ray scattering signal is non-centrosymmetric due to microscopic electron currents and cannot be straightforwardly related to the time-dependent electron density [44, 45]. It has been suggested that the centrosymmetric component of the signal correlates with the electron density [52]. However, this idea has not been elaborated upon further. In this study, we demonstrate how to observe the density of a coupled electron-hole using attosecond momentum-resolved RIXS.

We describe an experiment, in which a pump pulse excited a molecule into a coherent superposition of the excited singlet states  $|\Psi_n\rangle$  with a hole in HOMO orbitals and an electron in LUMO orbitals with corresponding eigenenergies  $\varepsilon_n$  creating an excited state  $\Psi(t) = \sum_{n \geq 1} C_n e^{-i\varepsilon_n t} |\Psi_n\rangle$ . Modern experimental capabilities make it possible to create such a coherent superposition of molecular excited states [24, 53–59]. An x-ray probe

pulse acts on the molecule after a nonzero time delay  $t_p$  and does not temporally overlap with the pump pulse. We consider the process in which an x-ray probe pulse is resonant to a transition of a core electron to energy levels below the Fermi level (see Fig. 1(a)). As these levels are occupied in the ground state, the scattering signal is primarily caused by excited molecules. This results in a substantial benefit of this method being unaffected by the background due to stationary electrons. We further assume that the x-ray pulse has a Gaussian-shaped temporal profile with duration  $\tau_p$  defined as the full width at the half maximum and has a bandwidth that is considerably larger than the energy splitting between the excited states involved in the dynamics, but smaller than

the energy difference between the ground and the excited states. The first condition is necessary to have a sufficient temporal resolution to resolve the excited-state dynamics. The latter condition is beneficial for the exclusion of the signal due to the interference with the ground state. The interference can appear, because the total wave function  $|\Psi^{(\text{tot})}\rangle = C_0 e^{-i\varepsilon_0 t_p} |\Psi_0\rangle + \sqrt{1 - |C_0|^2} |\Psi(t)\rangle$  includes a contribution from the ground state  $|\Psi_0\rangle$ .  $C_0$  is the corresponding complex expansion coefficient. Our assumption describes the experimental conditions, when a time-resolved signal is sensitive only to the excited-state dynamics and would not be distracted by the interference with the ground state. In Appendix B, we derive the scattering probability with these assumptions

$$P(\mathbf{Q}, t_p) = P_e P_0 \theta(\mathbf{n}_Q) \sum_F \frac{1}{\omega_s} \left| \sum_n C_n e^{-i\varepsilon_n t_p} e^{-\frac{(\varepsilon_F + \omega_s - \varepsilon_n - \omega_{\text{in}})^2 \tau_p^2}{8 \ln 2}} \sum_J e^{i\mathbf{Q} \cdot \mathbf{R}_J} \cdot \frac{\langle \Psi_F | \boldsymbol{\epsilon}_s^* \cdot \nabla | \Psi_J \rangle \langle \Psi_J | \boldsymbol{\epsilon}_{\text{in}} \cdot \nabla | \Psi_n \rangle}{(\omega_s + \varepsilon_F - \varepsilon_J + i\frac{\Gamma}{2})} \right|^2, \quad (1)$$

where  $P_e = 1 - |C_0|^2$  is the probability that the molecule is in an excited state and  $P_0$  is a constant prefactor.  $\mathbf{Q} = \mathbf{k}_s - \mathbf{k}_{\text{in}}$  is the scattered vector;  $\mathbf{k}_{\text{in}}$ ,  $\omega_{\text{in}}$ , and  $\mathbf{k}_s$ ,  $\omega_s$  denote the wave vector and photon energy of incoming and scattered radiation, respectively.  $\boldsymbol{\epsilon}_{\text{in}}$  is the polarization of the incoming pulse. Since photons are scattered in various possible directions, they have different polarizations, which leads to an additional dependence of the signal on the direction of the scattered vector  $\mathbf{n}_Q$  through the emission transition matrix elements. This dependence does not carry relevant information. We factored it out into  $\theta(\mathbf{n}_Q)$  by the application of a reflective polarizer for the polarization  $\boldsymbol{\epsilon}_s$ , please see Ref. [45] for details.  $|\Psi_J\rangle$  is the intermediate state with a hole at a localized core orbital at position  $\mathbf{R}_J$ . Its energy is denoted as  $\varepsilon_J$  and its lifetime broadening as  $\Gamma$ . The first sum runs over all possible final states  $|\Psi_F\rangle$  with energies  $\varepsilon_F$ . In the following analysis, we focus on such transitions that result in a scattered photon being close to the incoming photon energy (see Fig. 1(a)). In this case, a final state would either coincide with the ground state, one of states involved in the dynamics or some other valence-excited state. Any possible transition is inelastic, since the initial state is a nonstationary state. We use atomic units for this and the following equations.

We demonstrate the power of attosecond resonant inelastic x-ray scattering to reveal information about coupled electron-hole dynamics by considering scattering on the sexithiophene molecule shown in Fig. 1(b). Sexithiophene is noteworthy for optoelectronic applications due to its special optical properties governed by excitonic excited states [60–62]. We take into account many-body effects due to electron-hole coupling using the restricted active space configuration interaction (RASCI) method [63] implemented in the MOLCAS package [64]. We calculate eigenstates and eigenenergies of sexithiophene, and

use them to calculate the electron density and the scattering signal with Eq. (1) (see Appendix A for further computational details).

We assume that a pump pulse created a coherent superposition of the first three bright excited singlet states with the energies 3.8 eV, 4.6 eV and 5.4 eV at time  $t_p = 0$ . We set the ground-state energy to zero. Excited states with higher energies can be excluded from the superposition in the pump process, since they are energetically separated (see Fig. 1(a)). We select the coefficients  $C_1$ ,  $C_2$  and  $C_3$  to be equal to  $1/\sqrt{3}$ , which can be achieved by selecting the appropriate pump-pulse parameters. The conclusions of our study are independent of the specific choice of coefficients. We show the difference between  $\rho(\mathbf{r}, t)$  and the ground-state electron density at two different time delays in Figs. 2 (a) and (b). We also disentangle the hole and electron contributions to the differential electron density as described in Appendix B and show them below it.

We assume that the x-ray probe pulse has a mean photon energy  $\omega_{\text{in}} = 2490$  eV and a duration  $\tau_p = 300$  as, which corresponds to a bandwidth of 2.6 eV,  $\mathbf{k}_{\text{in}}||y$  and  $\boldsymbol{\epsilon}_{\text{in}}||x$ . Such an x-ray pulse is resonant with transitions from the states  $|\Psi_{1,2,3}\rangle$  to the intermediate states with a hole in the sulfur  $1s$  orbitals. The energies of the core-excited states of sexithiophene vary slightly depending on the location of the core hole, by no more than 120 meV. This forms groups of core-excited states, depending on the character of the excitations in the LUMO orbitals. We set  $\omega_{\text{in}}$  such that transitions to the lowest-energy group of core-excited states dominate, thus facilitating the analysis. The lifetime broadening of sulfur  $1s$ -excited states  $\Gamma$  is 0.59 eV [65].

Figure 1(c) shows momentum-unresolved spectra at two different time delays. The right intensive peak corresponds to emission into a final state that is the ground

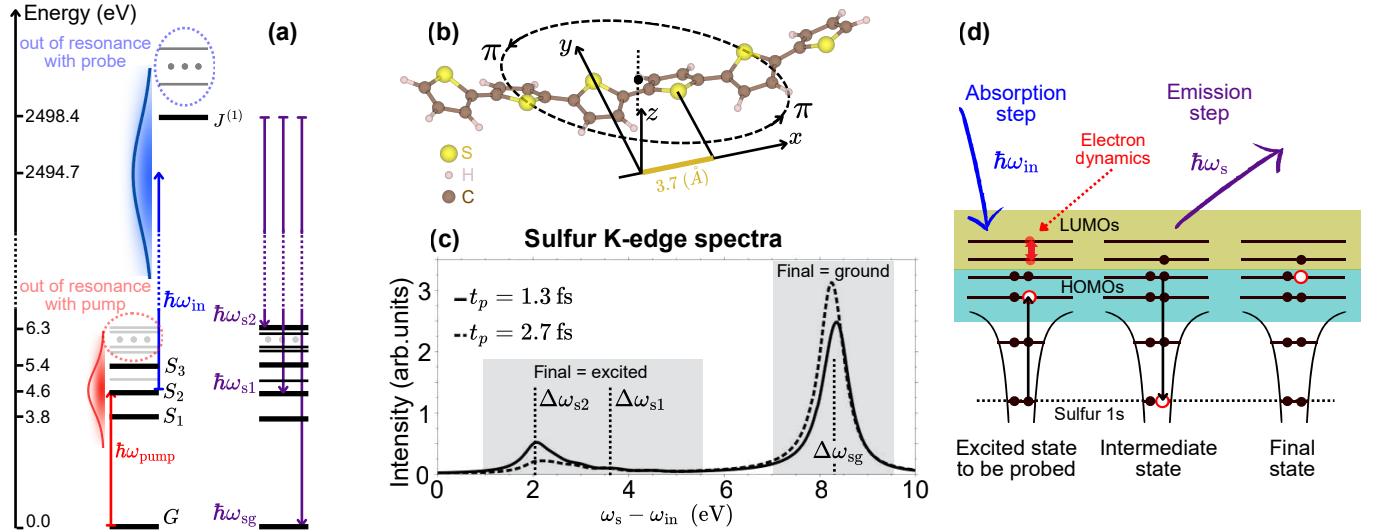


FIG. 1. (a) Illustration of attosecond pump-probe experiment. (b) Sexithiophene molecule. (c) Sulfur K-edge spectra of an excited sexithiophene molecule at different time delays ( $\mathbf{k}_{in}||y$ ,  $\epsilon_{in}||x$ ). (d) Illustration of states involved in the dynamics and transitions.

state. The peak is actually composed of several peaks. The positions of the individual peaks do not vary over time, but the intensity does, which leads to the illusion that the peak shifts. The left broad peak is due to emission with final states being valence excited states. The bandwidth of the individual peaks is determined by both the spectral bandwidth of the probe pulse and the Lorentzian lifetime broadening.

Figures 2 (c), (d), (f)-(i) show the centrosymmetric part of the time- and momentum-resolved RIXS signal,  $[P(\mathbf{Q}) + P(-\mathbf{Q})]/2$ , at the three different scattered energies outlined in Fig. 1 (c), and at different time delays. This part of the signal follows the electron density, since it involves the same interference terms  $\sum_{n_1, n_2 > n_1} \text{Re}(C_{n_2}^* C_{n_1} e^{-i(\varepsilon_{n_1} - \varepsilon_{n_2})t_p})$  as the density does [52]. Here, we apply the polarizer for  $\epsilon_s||z$  and divide the signal by  $\theta(\mathbf{n}_Q)$ . The total time- and momentum-resolved RIXS signal shown in the supplementary Fig. S1 is not centrosymmetric due to the presence of currents [44]. Since the intermediate states have localized holes on sulfur atoms, sulfur atoms are the scattering atoms. The  $\mathbf{Q}$ -dependent part of the signal is a combination of periodic functions with periods  $1/\lambda_{ik}$ , where  $\lambda_{ik} = |\mathbf{R}_i - \mathbf{R}_k|/2\pi$  with  $i$  and  $k$  denoting different sulfur atoms. The spatial resolution is sufficient to resolve oscillations due to nearest-neighbour sulfur atoms separated by 4.3 Å.

The scattering signal is sensitive to the excited-state dynamics through the time-dependent absorption amplitudes. During the absorption step of the scattering process, a core electron localized on a sulfur atom  $i$  fills the delocalized hole. This transition is only possible if the hole density around the atom  $i$  at the time of the measurement is considerable. Interference fringes in the scattering signal appear, if a pair of atoms scatters. Thus, maxima separated by  $1/\lambda_{ik}$  in the signal indicate that the

hole density is simultaneously non-zero around a pair of atoms  $i$  and  $k$ . For example, the hole density on the most widely separated atoms 1 and 6 is considerable at time  $t_p = 1.3$  fs (see Fig. 2 (a)). In contrast, the hole density on the atom 6 is negligible at time  $t_p = 2.7$  fs (see Fig. 2 (b)). Consequently, the shortest-period oscillations can clearly be observed in all momentum maps at  $t_p = 1.3$  fs, but are not visible in the maps at  $t_p = 2.7$  fs. The scattering signal, thus, encodes information about the hole density at the time of measurement.

It is also relevant to investigate the electron contribution to the excited-state dynamics. This contribution is due to the excited states having electrons distributed in the LUMO states. It turns out that the signal is also sensitive to this electron contribution, if the molecule's final state is the ground state. This connection is non-trivial, so let us explain it using the independent-particle picture. After the action of the probe pulse, a core electron is excited to a HOMO orbital, while the same LUMO orbital remains occupied after absorption (see Fig. 2(e)). During emission, the LUMO electron fills the core hole, placing the system in the ground state. For emission to be possible, a LUMO distribution on an atom must be considerable. Therefore, both an excited-state hole and electron distribution must be considerable around a scattering atom for scattering to be possible. A  $\lambda_{ik}$  oscillation in the corresponding signal reflects the simultaneous presence of an electron-hole pair on atoms  $i$  and  $k$ . The hole and electron distributions of optically-excited sexithiophene move almost synchronously, enhancing the contrast of the oscillations.

Now, let us consider transitions in which the final state is not the ground state, but rather a valence-excited state. Due to the same absorption step, the signal would still be sensitive to the excited-state hole density. How-

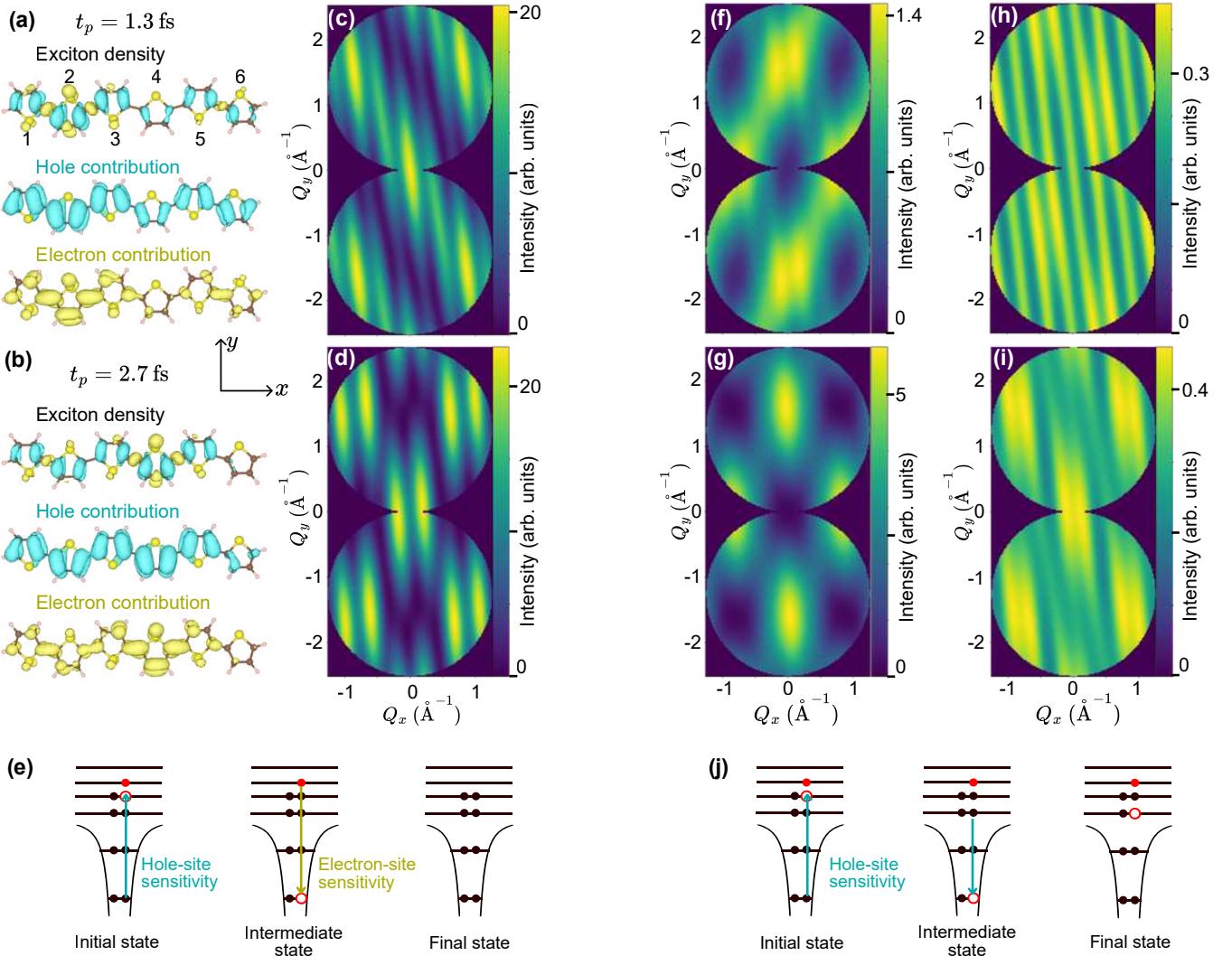


FIG. 2. (a) - (b) Exciton density, hole and electron contributions to the exciton density at (a)  $t_p = 1.3$  fs and (b)  $t_p = 2.7$  fs visualized with the VESTA package [66]. Yellow and cyan isosurfaces correspond to the negatively- and positively-charged regions. (c)–(d) The even part of the momentum maps at  $Q_z = 0$ ,  $[P(Q_x, Q_y, 0) + P(-Q_x, -Q_y, 0)] / (2\theta(\mathbf{n}_Q))$ , with the final state being the ground state at (c)  $t_p = 1.3$  fs and (d)  $t_p = 2.7$  fs and (e) illustration of the involved transitions. (f)–(i) The same as (c)–(d), but with the final state being a valence-excited state at (f)  $\omega_s - \omega_{in} = \Delta\omega_{s2}$  and  $t_p = 1.3$  fs; (g)  $\omega_s - \omega_{in} = \Delta\omega_{s2}$  and  $t_p = 2.7$  fs; (h)  $\omega_s - \omega_{in} = \Delta\omega_{s1}$  and  $t_p = 1.3$  fs; and (i)  $\omega_s - \omega_{in} = \Delta\omega_{s1}$  and  $t_p = 2.7$  fs. (j) Illustration of the scattering process with a final state being a valence-excited state.

ever, the connection to the electron contribution would not hold. We use the independent-particle picture again to illustrate this mechanism (see Fig. 2(j)). For absorption and subsequent emission to a final state being an excited state, all states involved must have the same LUMO orbital being occupied by an electron. This condition excludes some possible final states and the only role of the LUMO electron is now to select possible final states. Emission is due an electron from a HOMO orbital filling the core hole. The structure of this HOMO orbital determines whether the  $\mathbf{Q}$  dependence due to the hole distribution around scattering atoms is suppressed or enhanced as can be observed in Figs. 2 (f)–(i). Unlike the energetically separated ground state, the valence-excited

states are close in energy, making it impossible to disentangle the role of an individual final state in the signal. Nevertheless, analyzing the signal at such scattering energies is advantageous. For scattering with the final state being the ground state, interference fringes are possible, only if both excited-state electron and hole distributions are considerable around an atomic pair. If the signal is now analyzed at a different scattered energy, new interference fringes can occur. This would indicate that a considerable hole distribution exists around some atoms where the electron distribution is negligible.

We introduced a method to extract the information about the time-dependent charge density evolving due to coupled electron-hole dynamics with the momentum-

resolved RIXS. It is a powerful method due to the resonant enhancement of the signal from moving particles, and its orbital and site sensitivity.

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## Appendix A: Computational details

The calculations of the electronic states of the isolated sexithiophene molecule are performed using the MOLCAS software [64]. The molecular geometry has been taken from a molecular structure database PubChem [67]. To calculate the ground state, we use the Hartree-Fock approach [68] within the ANO-S-VTZP atomic orbital basis set [69]. We use these molecular orbitals without further optimization to obtain the excited states within the restricted active space configuration interaction (RASCI) method [70]. The RASCI method represents the excited state as a sum of configuration state functions (CSFs) [71]. We restrict the expansion to the singly excited CSFs, such that the molecular eigenstate is  $|\Psi_n\rangle = \sum_{i,a} c_{ia}^{(n)} |\Phi_i^a\rangle$ , where  $|\Phi_i^a\rangle$  denotes a CSF with a

hole in the  $i^{\text{th}}$  molecular orbital and an additional electron on the  $a^{\text{th}}$  molecular orbital. The calculations of the valence excited states converge with respect to the active space on 100 inactive orbitals, 27 RAS1 orbitals, and 27 RAS3 orbitals [72]. Calculating charge dynamics, we neglect the nuclear motion assuming that the coherence loss is negligible for the considered time scales of few femtoseconds [73–76].

We have compared our results with the available experimental data. In our calculations, the energy difference between the first excited state and the ground state is 3.8 eV. There are no data on the isolated molecules, but there are many experiments on sexithiophene in the solid phase and in various solutions. The first absorption peak appears at approximately 2.3 – 3.0 eV [77–82].

We calculate the core-excited intermediate states using the RASCI with the highly excited states (HEXS) method, following the procedure described in [83]. The first six molecular orbitals are predominantly represented as linear combinations of six sulfur 1s basis atomic orbitals. In six different calculations, we put one of these molecular orbitals into the RAS1 subspace. The RAS3 subspace is kept the same as for the valence-excited states (see the supplementary Fig. S2). Since the core molecular orbitals are delocalized, the core hole in the calculated excited state,  $J'$ , is also delocalized. The first six core-excited states are nearly degenerate in energy (the energy difference is less than 120 meV). This means that the states  $J'$  can be transformed into six states  $J$  with a

localized core hole. The state  $J'$  can then be expressed as a linear combination of the CSFs with a hole in the sulfur 1s molecular orbital  $j'$  and an electron in an unoccupied orbital  $b$ :  $|\Psi_{J'}\rangle = \sum_b c_b^{(J')} |\Phi_{j'}^b\rangle$ .

We express the field operators  $\hat{\psi}$  and  $\hat{\psi}^\dagger$  in the basis of the electron creation  $\hat{c}^\dagger$  and annihilation  $\hat{c}$  operators and rewrite the transition matrix elements between the valence and sulfur 1s-excited states in the basis of the CSFs:

$$\langle \Psi'_{J'} | \hat{\psi}^\dagger e^{i\mathbf{k}\cdot\mathbf{r}} (\epsilon \cdot \nabla) \hat{\psi} | \Psi_n \rangle = \sum_{p,q} \sum_{a,i,b} c_b^{(J')} {}^* c_{ia}^{(n)} \\ \times \langle \Phi_{j'}^b | \hat{c}_p^\dagger \hat{c}_q | \Phi_i^a \rangle \langle \phi_p | e^{i\mathbf{k}\cdot\mathbf{r}} \epsilon \cdot \nabla | \phi_q \rangle, \quad (A1)$$

where the matrix element  $\langle \Phi_{j'}^b | \hat{c}_p^\dagger \hat{c}_q | \Phi_i^a \rangle$  is nonzero only if the two configurations differ by at most one occupied orbital. Since the molecular orbital  $\phi_{j'}$  corresponds to the sulfur 1s orbital, which is doubly occupied in the configuration  $|\Phi_i^a\rangle$  and singly occupied in  $|\Phi_{j'}^b\rangle$ , the annihilation operator  $\hat{c}_q$  yields a nonzero value only when  $q = j'$ . We expand the molecular orbital as a linear combination of the basis atomic orbitals,  $|\phi_{j'}\rangle = \sum_{N,o} \Xi_{j',N,o} |\xi_{N,o}\rangle$ . Here,

$o$  denotes the index of the basis atomic orbital of the atom  $N$ . For the first six molecular orbitals  $j'$ , the coefficients  $\Xi_{j',N,o}$  are significant only for strongly localized sulfur 1s atomic orbitals. Assuming that the x-ray wavelength is much larger than the spatial extend of the 1s-orbital leads to the approximation  $e^{i\mathbf{k}\cdot\mathbf{r}} \Xi_{j',N,o} |\xi_{N,o}\rangle \approx e^{i\mathbf{k}\cdot\mathbf{R}_N} \Xi_{j',N,o} |\xi_{N,o}\rangle$ . The transition matrix element can then be expressed then as

$$\langle \phi_p | e^{i\mathbf{k}\cdot\mathbf{r}} (\epsilon \cdot \nabla) | \phi_{j'} \rangle = \sum_{N,o} \Xi_{j',N,o} \langle \phi_p | e^{i\mathbf{k}\cdot\mathbf{r}} (\epsilon \cdot \nabla) | \xi_{N,o} \rangle \\ \approx \sum_{N,o} \Xi_{j',N,o} e^{i\mathbf{k}\cdot\mathbf{R}_N} \langle \phi_p | \epsilon \cdot \nabla | \xi_{N,o} \rangle. \quad (A2)$$

## Appendix B: Equation derivation

The general expression for attosecond momentum-resolved RIXS has been derived in Ref. [44] using the time-dependent second-order perturbation theory and the second quantization formalism. In the present work, we follow the same derivation steps, but (i) do not integrate the signal over the energy window and (ii) do not apply the mean energy approximation for the non-stationary electronic system.

We first show that the scattering probability does not have a background due to the ground state. If the initial state is  $|\Psi^{(\text{tot})}\rangle$ , the scattering probability can be expressed as a function of the probe pulse parameters

$\omega_{\text{in}}$  and  $\tau_p$  [44]:

$$P(\omega_{\text{in}}, \tau_p) = a \sum_{F, s_s} \left| C_0 e^{-\frac{(\varepsilon_F + \omega_s - \varepsilon_0 - \omega_{\text{in}})^2 \tau_p^2}{8 \ln 2}} b_{0,F} \right. \\ \left. + \sum_{n \geq 1} \sqrt{1 - |C_0|^2} C_n e^{-\frac{(\varepsilon_F + \omega_s - \varepsilon_n - \omega_{\text{in}})^2 \tau_p^2}{8 \ln 2}} b_{n,F} \right|^2, \quad (\text{B1})$$

where coefficients  $a$  and  $b_{n,F}$  depend neither on  $\omega_{\text{in}}$  nor on  $\tau_p$ . The first term in the modulus is the contribution of the ground state to the scattering signal. Since in our case, the energy difference between the ground state and any excited state is much larger than the energy difference between any two excited states, the factor  $(\varepsilon_F + \omega_s - \varepsilon_0 - \omega_{\text{in}})$  in the exponent in the first term is considerably larger than that in the other terms,  $(\varepsilon_F + \omega_s - \varepsilon_n - \omega_{\text{in}})$ , for any  $n \geq 1$ . Consequently, the exponent in the first term is much smaller than those in the

others. For our parameters  $\tau_p = 300$  as,  $\omega_{\text{in}} = 2490$  eV, it is approximately ten times smaller. Therefore, we neglect the first term, and express the scattering probability as:

$$P(\omega_{\text{in}}, \tau_p) \approx a P_e \sum_{F, s_s} \left| \sum_{n \geq 1} C_n e^{-\frac{(\varepsilon_F + \omega_s - \varepsilon_n - \omega_{\text{in}})^2 \tau_p^2}{8 \ln 2}} b_{n,F} \right|^2, \quad (\text{B2})$$

where  $P_e = (1 - |C_0|^2)$  is the probability that the system is in an excited state. The contribution of the ground state is now in the pre-factor  $P_e$ .

Using the approximation in Eq. (A2) for the transition matrix element in Eq. (A1) and the approximation in Eq. (B2), we obtain the following expression for the attosecond momentum-resolved RIXS signal:

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$$P(\mathbf{k}_s, t_p) = P_e \theta(\mathbf{n}_Q) P_0 \sum_F \frac{1}{\omega_s} \left| \sum_n C_n e^{-i\varepsilon_n t_p} e^{-\frac{(\varepsilon_F + \omega_s - \varepsilon_n - \omega_{\text{in}})^2 \tau_p^2}{8 \ln 2}} \sum_{J'} \frac{1}{(\omega_s + \varepsilon_F - \varepsilon_{J'} + i\frac{\Gamma}{2})} \right. \\ \times \left( \epsilon_s^* \cdot \sum_{p_1, q_1} \sum_{N_1, o_1} e^{-i\mathbf{k}_s \cdot \mathbf{R}_{N_1}} \Xi_{p_1, N_1, o_1}^* \langle \xi_{N_1, o_1} | \nabla | \phi_{q_1} \rangle \langle \Psi_F | \hat{c}_{p_1}^\dagger \hat{c}_{q_1} | \Psi'_{J'} \rangle \right) \\ \times \left. \left( \epsilon_{\text{in}} \cdot \sum_{p_2, q_2} \sum_{N_2, o_2} e^{i\mathbf{k}_{\text{in}} \cdot \mathbf{R}_{N_2}} \Xi_{q_2, N_2, o_2} \langle \phi_{p_2} | \nabla | \xi_{N_2, o_2} \rangle \langle \Psi'_{J'} | \hat{c}_{p_2}^\dagger \hat{c}_{q_2} | \Psi_n \rangle \right) \right|^2, \quad (\text{B3})$$


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where  $P_0 = 2\pi^3 I_0 \tau_p^2 / (\ln 2 c V \omega_{\text{in}}^2)$  with  $I_0$  being the peak intensity of the probe pulse,  $c$  - the speed of light, and  $V$  - the quantization volume.

As explained in Appendix A, we represent the state  $|\Psi_J\rangle$  with a hole localized on a single sulfur atom  $j$  as a linear combination of the calculated intermediate states  $|\Psi_J\rangle \approx \sum_{j'} \alpha_{jj'} |\Psi'_{J'}\rangle$ . Under this approximation, Eq. (1) can be obtained from Eq. (B3). We have checked that the scattering probabilities calculated with and without this assumption differ by less than 1%.

During the excitation process, the absorption of an UV photon creates an electron-hole pair. Consequently, the charge density of the excited state  $\rho = |\Psi(t)|^2$  differs from that of the ground state  $\rho_G$  by one hole in the RAS1 space (HOMOs) and one electron in the RAS3 space (LUMOs). We denote this difference by the exciton density. The exciton density has the contribution due the LUMOs electron density  $\rho_e(t_p)$  and the HOMOs hole density  $\rho_h(t_p)$ , which we disentangle with the procedure below:

$$\rho(t_p, \mathbf{r}) - \rho_G(\mathbf{r}) = \rho_e(t_p) + \rho_h(t_p) = \sum_{m,n} C_m^* C_n e^{i(\varepsilon_m - \varepsilon_n)t_p} \sum_{p,q} \langle \Psi_m | \hat{c}_p^\dagger \hat{c}_q | \Psi_n \rangle \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) - \sum_{p \in \text{HOMOs}} |\phi_p(\mathbf{r})|^2, \\ \rho_e(t_p) = 2 \text{Re} \left( \sum_{m,n \geq m} C_m^* C_n e^{i(\varepsilon_m - \varepsilon_n)t_p} \sum_{p,q \in \text{LUMOs}} \langle \Psi_m | \hat{c}_p^\dagger \hat{c}_q | \Psi_n \rangle \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) \right), \quad (\text{B4})$$

$$\rho_h(t_p) = 2 \text{Re} \left( \sum_{m,n > m} C_m^* C_n e^{i(\varepsilon_m - \varepsilon_n)t_p} \sum_{p,q \in \text{HOMOs}} \langle \Psi_m | \hat{c}_p^\dagger \hat{c}_q | \Psi_n \rangle \phi_p^*(\mathbf{r}) \phi_q(\mathbf{r}) \right). \quad (\text{B5})$$

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## Supplemental Material for "Attosecond momentum-resolved resonant inelastic x-ray scattering for imaging coupled electron-hole dynamics"

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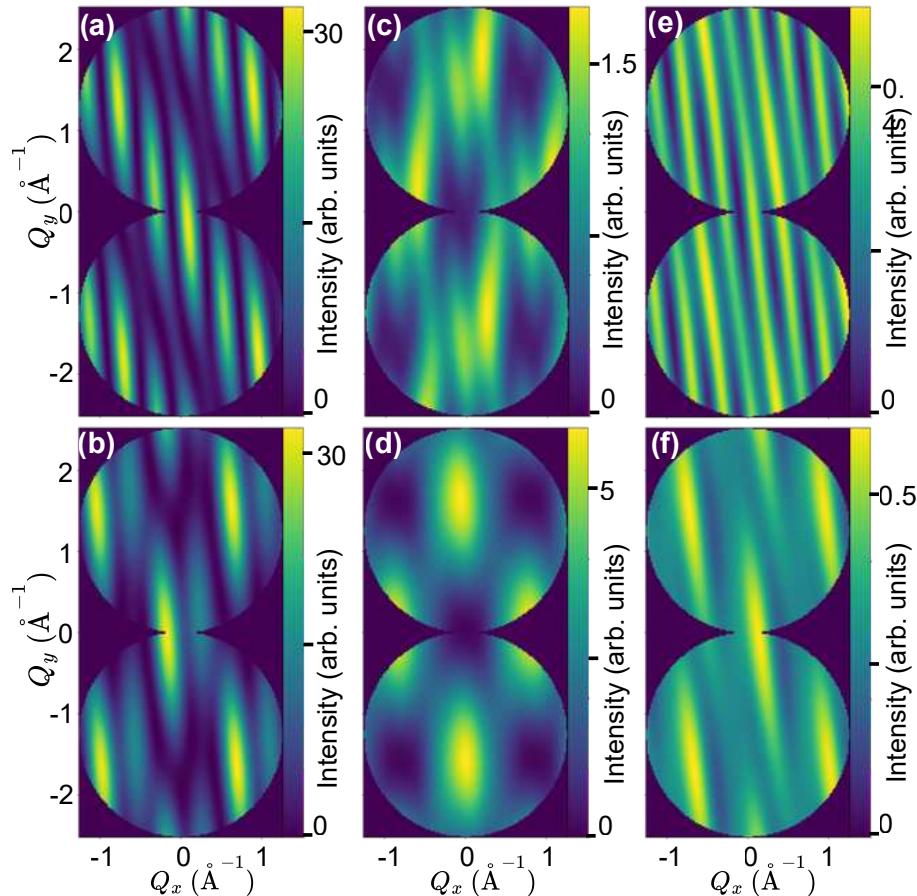


FIG. S1. The momentum maps  $P(Q_x, Q_y, 0)/(\theta(n_Q))$  at  $Q_z = 0$ , with the final state being the ground state at (a)  $t_p = 1.3$  fs and (b)  $t_p = 2.7$  fs. (c)–(f) The same as (a)–(b), but with the final state being a valence-excited state at (c)  $\omega_s - \omega_{\text{in}} = \Delta\omega_{s2}$  and  $t_p = 1.3$  fs; (d)  $\omega_s - \omega_{\text{in}} = \Delta\omega_{s2}$  and  $t_p = 2.7$  fs; (e)  $\omega_s - \omega_{\text{in}} = \Delta\omega_{s1}$  and  $t_p = 1.3$  fs and (f)  $\omega_s - \omega_{\text{in}} = \Delta\omega_{s1}$  and  $t_p = 2.7$  fs.

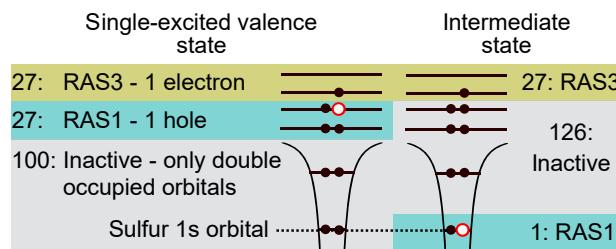


FIG. S2. Restricted active spaces for calculations of the valence-excited and 1s-excited states.