ABSTRACT: Time-resolved, resonant X-ray sum-frequency generation in aligned selenophene molecules is calculated. A wave packet of valence-excited states, prepared by an extreme-ultraviolet pump pulse, is probed by two 12-keV X-ray probe pulses resonant with the Se core-excited states for variable time delays. At these hard-X-ray frequencies, the angstrom wavelength of the X-ray probe is comparable to the molecular size. We thus employ a nonlocal description of the light–matter interaction based on the minimal-coupling Hamiltonian. The wavevector-resolved resonant stimulated sum-frequency-generation signal, obtained by varying the propagation direction of hard-X-ray pulses, can thus directly monitor the transition current densities between core and ground/valence states. This is in contrast to off-resonant diffraction, which detects the transition charge densities.

1. INTRODUCTION

Recent advances in the generation of bright, coherent X-ray pulses by high-order harmonic generation and free-electron lasers (FELs) are enabling time- and space-resolved X-ray spectroscopy of molecules involving electronic core-excited states. Core electrons have element-specific transition energies and are strongly localized around a given atom. By tuning an X-ray pulse to a desired core, it is thus possible to monitor a specific region of the molecule. In recent experiments, X-ray FEL pulses have been used to directly access the evolution of the core-excited states or to generate a localized superposition of valence states via stimulated X-ray Raman scattering for probing the charge migration of a superposition of electronic states in a molecule or the long-range charge and energy transfer in molecular aggregates.

The implementation of optical–X-ray wave mixing in multidimensional nonlinear X-ray spectroscopy constitutes a major challenge. Nonlinear wave mixing of infrared and visible pulses, such as sum-frequency generation (SFG), has long been applied to molecular vibrational spectroscopy. The extension to X-ray frequencies was proposed in refs 13 and 14, but optical–X-ray SFG and optical–XUV four-wave mixing could only recently be demonstrated at FEL light sources.

Time-resolved X-ray sum-frequency diffraction was recently put forward to access the evolution of the transition charge densities. In this process, a superposition of valence or core-excited states, generated by a resonant XUV or X-ray pump pulse, respectively, is probed by two off-resonant X-ray pulses with time, frequency, and wavevector resolution. This is an SFG extension of time-resolved X-ray diffraction, which is currently applied for the reconstruction of time-dependent charge and current densities.

When the X-ray probe pulse is tuned to a core K-edge, time-resolved resonant X-ray SFG offers selectivity of valence dynamics via element-specific core transitions. In ref 26, resonant X-ray SFG in acetyl fluoride has been shown to provide selectivity by tuning an X-ray probe pulse to the F and O K-edges, thereby revealing which regions of the molecule contribute to the X-ray excitation. At those frequencies, which span a few hundreds of electronvolts, the X-ray pulse wavelength is long compared to the molecular size, and the signal does not depend on the propagation direction of the pulses.

Here, we investigate stimulated X-ray SFG in aligned selenophene molecules, using 12-keV X-ray probe pulses resonant with the Se core-excited states. Selenophene is a planar ring molecule, shown in Figure 1a, containing a Se atom with hard-X-ray core transitions. The associated X-ray wavelength is smaller than the molecular size, rendering the dipole approximation inapplicable and requiring a nonlocal description of the light–matter interaction based on the minimal-coupling interaction Hamiltonian. Selenophene is thus a good candidate to probe delocalized molecular charge densities.
current densities by nonlinear X-ray signals. In contrast to previous off-resonant \(^{17-19}\) and resonant \(^{26}\) X-ray SFG studies, here, we investigate wavevector-resolved stimulated X-ray SFG for resonant, angstrom-wavelength pulses. By varying the X-ray probe propagation direction, we find observable changes in the SFG peak strengths, which can be ascribed to the spatial dependence of the transition current densities in the molecule. This allows one to experimentally reconstruct the space-dependent molecular X-ray couplings.

2. THEORETICAL MODEL

The stimulated X-ray SFG pulse configuration is displayed in Figure 1. A resonant XUV pump pulse prepares a superposition of valence-excited states, which is probed after a time delay \(T\) by two time-coincident resonant X-ray pulses, inducing a Raman transition from the valence states \(e\) to the ground state \(g\) via the core-excited states \(f\). The SFG signal is obtained by detecting the spectrum of the transmitted X-ray pulse \(X\). For temporally well separated XUV pump and X-ray probe pulses, the signal reads

\[
\hat{A}(\omega) = \int dt \hat{A}(t) e^{i\omega t}
\]

which are centered on \(\omega = 0\). Atomic units are used in the following, unless stated otherwise.

The stimulated SFG signal is calculated using the minimal-coupling radiation–matter interaction Hamiltonian \(^{27,28}\)

\[
\hat{H}_{\text{int}}(t) = -\int d^3r \hat{j}(r) \cdot \hat{A}(r, t)
\]

where \(\hat{j}(r)\) is the electronic current-density operator and \(\hat{A}(r, t) = A_{\text{XUV}}(r, t) + A_{\text{X1}}(r, t) + A_{\text{X2}}(r, t)\) is the total vector potential. This nonlocal description, which avoids the multipole expansion of the light–matter interaction, fully accounts for the spatial variation of the short-wavelength X-ray pulses within the molecule. In eq 3, we assumed resonant excitations and thus neglected the contribution of the electronic charge-density operator \(\hat{\sigma}(r)\), which would be dominant for off-resonant excitations. \(^{26}\) The stimulated SFG signal is obtained by measuring the spectrum of the transmitted X-ray pulse

\[
A_{\text{XUV}}(r, t) = A_{\text{XUV}}(r, t) + A_{\text{X1}}(r, t) + A_{\text{X2}}(r, t)
\]

where \(A_{\text{XUV}}(r, t)\) is justiﬁed for \(T\) well separated XUV pump and X-ray probe pulses, the signal explicitly depends upon the propagation direction \(k_H\) via the transition current densities

\[
\hat{j}_{ab}(k) = \int d^3r \hat{j}_{ab}(r) e^{ikr}
\]

where the indices \(a\) and \(b\) in the matrix elements \(A_{ab} = \langle a|\hat{A}|b\rangle\) run over the core and valence/ground states. For temporally well separated XUV pump and X-ray probe pulses, the signal reads

\[
S(\omega_f, T, k_X) = 2\text{Im} \sum_{i,j} \hat{A}_{X1}(\omega_i - \omega_X) \\
\times \hat{A}_{X2}(\omega_i - \omega_X) \\
\times \hat{A}_{\text{XUV}}(\omega_f - \omega_X) - i\hat{j}_{ab}(k_X)\hat{\varepsilon}_{X1}(k_{\text{XUV}})\hat{\varepsilon}_{X2}(k_X)
\]

where we sum over the valence \((e)\) and core \((f)\) states, including the associated decay rates \(\gamma_e\) and \(\gamma_f\) and transition energies \(\omega_e\) and \(\omega_f\) to the ground state. For the XUV pulse, \(\hat{j}_{ef}(k_{\text{XUV}}) \approx \hat{j}_{ef}(0)\), and the transition matrix elements reduce to the dipole couplings in the dipole approximation. We notice that modeling the X-ray probe pulses as plane waves with a well-deﬁned value of \(|k_X| = \omega_X/c\) is justiﬁed in our case, since the transition current densities \(\hat{j}_{ab}(k)\) depend on the
The SFG signal strength is determined by the intensity of the X-ray probe pulses and the molecular density. Sufficiently low intensities are needed to realize the perturbative approach schematically shown in Figure 1b and to reduce the influence of competing effects, such as X-ray photoionization and population losses, which are not included here and can alter the molecular response \((j^{\text{SFG}}(r,t))\) in eq 18. While this restricts the range of utilizable X-ray intensities in an experiment, the SFG signal strength can still be maximized by a suitable choice of the molecular density. Optical–X-ray SFG\(^{15}\) and optical–XUV four-wave mixing\(^{16}\) have been observed experimentally at FELs. Stimulated resonant X-ray Raman scattering, the process on which the proposed SFG setup relies, was successfully demonstrated in neon\(^7\) thanks to the amplification of the signal through the medium. In molecules, detecting signatures of stimulated Raman scattering in the transmitted X-ray pulse spectrum has proved challenging.\(^{30}\) Stimulated X-ray Raman scattering was recently observed in NO molecules by measuring the resulting electronic population transfer with a second XUV pulse\(^8\) and not by directly detecting the absorbed photons. As we discuss in Appendix B, distinguishing the SFG spectrum has proved challenging.\(^{30}\) Stimulated X-ray Raman scattering in the transmitted X-ray pulse gives the energy and line width of the core states in the frequency-resolved spectrum, the dependence of which on the transition current densities in eqs 4–7 are finally given by

\[
\begin{align*}
\hat{j}(r) &= \sum_{\mu,\nu} D_{\mu \nu} e^{i(\Omega \cdot r)} \\
\hat{j}_{\mu}(r) &= \frac{1}{2} [\chi_{\mu}^*(r) \nabla \chi_{\nu}(r) - \chi_{\nu}^*(r) \nabla \chi_{\mu}(r)]
\end{align*}
\]

\[
\alpha_{\text{XUV}}(t) = \alpha_{\text{XUV},0} e^{-t^2/(2\tau_{\text{XUV}}^2)}
\]

\[
\alpha_{\text{XUV}}(\omega) = \sqrt{2\pi} \tau_{\text{XUV}} \alpha_{\text{XUV},0} e^{-(\omega_{\text{XUV}} - \omega_0)^2/2}
\]

with duration \(\tau_{\text{XUV}} = 200\) as, carrier frequency \(\omega_{\text{XUV}} = 9\) eV, and linear polarization \(\hat{e}_{\text{XUV}} = \hat{e}_z\) along the z direction. Such
broadband pulse generates a large superposition of valence states, even though this is not a requirement for the observation of signatures of delocalized current densities in the SFG signal. If needed, a broad superposition of valence states could also be produced by the stimulated Raman scattering of a broadband X-ray pulse. Alternatively, a narrower XUV pump pulse could be used to excite a few selected valence states of interest. The eg coherence generated by the pump is subsequently probed by the two broadband Gaussian X-ray pulses,

$$A_{X_0}(t) = A_{X_0,0} e^{-t^2/(2 \tau_{X_0}^2)}$$

$$A_{X_0}(\omega) = \sqrt{2 \pi} \tau_{X_0} A_{X_{0,0}} e^{-(\omega_{X_0} \gamma)^2/2}$$

where \( n \in \{1, 2\} \), both with duration \( \tau_{X_0} = 100 \) as and carrier frequencies \( \omega_{X1} = 12.65 \) keV and \( \omega_{X2} = 12.66 \) keV. Such broad 10 eV bandwidths, enabling the excitation of a large number of core states, are achievable with X-ray FELs, especially with recently demonstrated FEL attosecond pulses. The carrier frequencies used ensure that the X1 and X2 pulses are resonant with the \( j \) eg transitions, respectively. The peak strengths \( A_{X_{UV}} \) and \( A_{X_{0,0}} \) act as multiplication constants in the signals of eqs 5 and 7. The spectra are displayed in arbitrary units in the following, and the experimental signal-to-background ratio is estimated in Appendix B.

The transition energies \( \omega_{eg} \) and \( \omega_{fg} \) and the elements \( D_{eg}^{fg} \) of the one-electron transition density matrix were obtained with CASSCF calculations. The lifetime broadening of the Se core-excited states in \( \gamma_f = 1.16 \) eV, and we set \( \gamma_{eg} = 0.05 \) eV for the valence-excited states. The two-dimensional SFG spectra shown in Figures 2 and 3 exhibit peaks along the \( \Omega \) and \( \omega_s \) axes, centered at the transition energies \( \omega_{eg} \) and \( \omega_{fg} \), respectively, and revealing the couplings between the valence- and core-excited states involved in the Raman excitation process (see also eq 7). These couplings can be controlled by varying the propagation direction \( k_X \) of the X-ray probe pulses. A first consequence of modifying the X-ray pulse propagation direction is the ensuing change of the polarization vectors \( \hat{\epsilon}_{X0} \) which are perpendicular to \( k_{X0} \), and the directions of which vary when \( k_{X0} \) moves out of a given plane. The polarization vectors \( \hat{\epsilon}_{Xn} \), determine which components of \( j_{fg}^{(-k_X)} \) and \( j_f^{k_X} \) in eq 7 contribute to the signal, with observable modifications in the SFG spectra.

Figure 2 depicts the SFG signal when the two X-ray pulses are linearly polarized along \( \hat{\epsilon}_X = \hat{\epsilon}_Y \) as shown in Figure 2a. The two-dimensional spectrum in Figure 2b was calculated for a propagation direction \( k_X \) along the \( x \) axis. The peaks along the \( \Omega \) and \( \omega_s \) axes are centered on the transition energies \( \omega_{eg} \) and \( \omega_{fg} \), respectively, which are marked by the horizontal and vertical lines. The role of different Se core-excited states is highlighted in Figure 2c, which displays a section of the two-dimensional spectrum evaluated at the frequency \( \Omega = \omega_{eg} = 7.11 \) eV of the third valence-excited state \( \epsilon_3 \). Two X-ray peaks are clearly visible, centered at the frequencies \( \omega_3 = \omega_{fg} = 126657 \) eV and \( \omega_3 = \omega_{fg} = 12664 \) eV of the second and ninth core-excited state, \( f_2 \) and \( f_9 \), respectively. An additional peak at \( \Omega = \omega_{eg} = 10.7 \) eV and \( \omega_3 = \omega_{fg} = 12657 \) eV is also apparent.

For linearly polarized X-ray pulses with \( \hat{\epsilon}_X = \hat{\epsilon}_Z \) as shown in Figure 3a, Figure 3b depicts the associated SFG spectrum evaluated for a propagation direction \( k_X \) along the \( z \) axis. As a result of different couplings, some of the peaks previously visible in Figure 2b are now suppressed, such as those centered at \( \Omega = \omega_{eg} = 10.7 \) eV or at \( \omega_3 = \omega_{fg} = 12664 \) eV. This is more clearly evinced by Figure 3c, where the section of the spectrum evaluated at \( \Omega = \omega_{eg} = 7.11 \) eV shows a single main peak centered on \( \omega_3 = \omega_{fg} = 12657 \) eV.

3.3. Nonlocal Molecular Properties Accessed by Wavevector-Resolved Resonant X-ray SFG. When varying \( k_X \) within a given plane, holding the polarization vector fixed as
shown, for example, in Figures 2a and 3a, the dependence of \( j_{f_{1}}(k_{x}) \) and \( j_{f_{2}}(k_{x}) \) on the X-ray pulse propagation direction produces observable variations in the resonant X-ray SFG signal. These arise from the short wavelength of the X-ray pulses, which renders them sensitive to spatial features within the molecule. Observing the dependence on the direction of \( k_{x} \) would require high-order multipoles and is readily captured by a nonlocal minimal-coupling formulation in terms of space-dependent current densities \( j(r) \).

In Figure 4, we depict the dependence of the main peak of Figure 3 on the X-ray pulse propagation direction. As shown in Figure 3a, we assume a wavevector \( k_{x}(\theta) = |k_{x}|[\cos(\theta)\hat{x}_{x} + \sin(\theta)\hat{y}_{x}] \) rotating in the \( xz \) plane, with fixed polarization along \( \hat{z}_{x} \). The \( \theta \) dependence of the peak in Figure 3c is highlighted in Figure 4a by displaying the difference between the spectra evaluated at a given \( \theta \) and at \( \theta = \pi/2 \). Figure 4a depicts sections of the spectra evaluated at \( \Omega = \omega_{eg} = 7.11 \) eV for discrete values of \( \theta \), whereas Figure 4b presents the complete \( \theta \) dependence of the peak at \( \Omega = \omega_{eg} = 7.11 \) eV and \( \omega_{e} = \omega_{f_{1}g} = 12657 \) eV. A significant change in the strength of this SFG peak is visible.

The peak in Figures 3 and 4 originates from the \( g \rightarrow f_{1} \rightarrow f_{2} \rightarrow g \) pathway associated with specific valence (\( e_{s} \)) and core (\( f_{2} \)) excited states. Figures 5 and 6 show the \( r \) and \( k \) dependence of the transition current densities involved in the above pathway. As visible in Figure 5a, the transition current density \( j_{f_{2}}(r)\hat{z}_{x} \), with \( r \) lying in the \( xz \) plane, is mostly peaked at the Se site, where the resonant core-excited states are localized. Figure 5a also shows additional, weaker current densities at the C sites. Due to their short wavelengths, the probe X-ray pulses encounter a different current density depending on their propagation directions. This can be better observed in \( k \) space, as shown in Figure 5b. For a given \( k_{x} \), the coupling due to an X-ray pulse in the \( k_{x}k_{z} \) plane is determined by the transition current densities \( j_{f_{2}}(k)\hat{z}_{x} \) varying along the black circle in Figure 5b. Its dependence on the X-ray incident angle \( \theta \) is displayed in Figure 5c.

Similar properties are featured by the transition current density \( j_{f_{2}}(r)\hat{z}_{x} \) between the valence- and core-excited states involved in the pathway, as apparent in Figure 6. Also in this case, the transition current density is mostly localized at the Se site, with additional contributions mostly around two of the four C sites. The associated transition current density \( j_{f_{2}}(k)\hat{z}_{x} \)
The spectra shown in Figures 3 and 4 are determined by the transition current densities involved in each step along the \( g \rightarrow e_3 \rightarrow f_2 \rightarrow g \) pathway. Figure 7 displays the product of these three transition couplings: \( j_{\beta \gamma}(r) \cdot \hat{z}_y \), \( j_{\beta \gamma}(k_{XUV}) \cdot \hat{z}_y \), and \( j_{\beta \gamma}(k_{X}(\theta)) \cdot \hat{z}_y \). While the first dipole coupling due to XUV excitation is not sensitive to the spatial features of the molecule, the subsequent transition current densities are clearly dependent on the incident angle \( \theta \) of the X-ray pulses. The product of transition couplings in Figure 7 exhibits the same dependence on \( \theta \) as the SFG spectrum in Figure 4b. This shows that wavevector-resolved resonant SFG can directly access nonlocal couplings and space-dependent transition current densities, when resonant X-ray pulses of short wavelength are used. This suggests interesting prospects for the direct reconstruction of space-dependent current densities in molecules.

4. DISCUSSION

Stimulated X-ray Raman excitations offer selectivity over electronic wave packets in molecules. By tuning X-ray pulses to
the element-specific core transitions of different atoms in the molecule, the motion of the electronic charge between different points can be followed. For hard-X-ray transition energies such as for Se core-excited states, the short wavelength of the X-ray pulses can be comparable to the molecular size. In such a case, a multipolar expansion of the light–matter interaction Hamiltonian, in terms of electric and magnetic multipoles accounting for the global properties of the molecule, would require high-order multipoles. The interaction of the molecule with resonant X-ray pulses is fully characterized by the space-dependent current densities, which can be observed in the X-ray spectra.

We have employed a nonlocal-response formalism based on gauge-invariant current-density operators and the minimal-coupling interaction Hamiltonian to calculate stimulated X-ray SFG of aligned selenophene molecules. Previous works had computed valence and core contributions to the transition current densities involving the Se core. A stimulated hard-X-ray SFG signal directly provides the transition current densities in Figures 3 and 4, with $k_0 = |k_0|[(\cos(\theta)\hat{e}_x + \sin(\theta)\hat{e}_y)]$ rotating in the $xz$ plane.

**Figure 7.** Modulus of the product of the transition current densities $j_{\mu}^{(\pm)}(-k_0(\theta))\hat{e}_{\pm}^{\mu}j_{\nu}^{(+)}(k_0(\theta))\hat{e}_{\nu}^{\nu}j_{\rho}^{(\pm)}(k_{\rho}^{\pm})\hat{e}_{\rho}$ which determines the spectra of Figures 3 and 4, with $k_0(\theta) = |k_0|[(\cos(\theta)\hat{e}_x + \sin(\theta)\hat{e}_y)]$ rotating in the $x$ $z$ plane.

**APPENDIX A. DERIVATION OF THE SFG SIGNAL**

The SFG signal is defined as the integrated rate of change of the number $N_{XUV}^2$ of photons in a mode $k$ with frequency $\omega_k$:

$$S(\omega_k) = \int dt \left( \frac{dN_{XUV}^2}{dt} \right)$$

(12)

For the heterodyne detection assumed here, the superscript $X2$ implies that the signal modes are restricted to those already occupied by the X-ray probe pulse $A_{X2}(r, t)$. The photon-number rate of change is obtained by applying Heisenberg’s equations of motion with the minimal-coupling interaction Hamiltonian in the rotating-wave approximation

$$H_{\text{int}} = -\sum_{\lambda} \int d^3r \left( \hat{\mathbf{A}}_{k,\lambda}(r) \hat{a}_{k,\lambda} + \hat{\mathbf{A}}_{k,\lambda}^*(r) \hat{a}_{k,\lambda}^\dagger \right)$$

(13)

Here, we define the positive- and negative-frequency contributions to the current density

$$\hat{j}(r) = \hat{j}^{(+)}(r) + \hat{j}^{(-)}(r)$$

(14)

and the vector-potential operator

$$\hat{\mathbf{A}}(r) = \sum_{k,\lambda} \hat{\mathbf{A}}_{k,\lambda}(r) \hat{a}_{k,\lambda} + \sum_{k,\lambda} \hat{\mathbf{A}}_{k,\lambda}^*(r) \hat{a}_{k,\lambda}^\dagger$$

(15)

We further denote the creation ($\hat{a}_{k,\lambda}$) and annihilation ($\hat{a}_{k,\lambda}^\dagger$) operators of a photon in a mode $k$ and polarization $\hat{e}_k$, and the coefficient

$$A_{k,\lambda}(r) = \sqrt{\frac{2\pi}{V_\omega \omega_k}} e^{i k_r r \hat{e}_k}$$

(16)

for a field quantization volume $V_\omega$. This leads to

$$\frac{dN_{X2}}{dt} = i \int d^3r \left[ \hat{\mathbf{A}}_{X2}(r) \hat{A}_{X2}^\dagger + \hat{\mathbf{A}}_{X2}^\dagger \hat{A}_{X2} - \text{H.c.} \right]$$

(17)

and the signal thus reads

$$S(\omega_k) = -2\text{Im} \left\{ \hat{\mathbf{A}}_{X2}^{\dagger}(\omega_k - \omega_{X2}) \times \int dt \int d^3r \left[ \hat{j}^{(-)}(r, t) \cdot \hat{\mathbf{e}}_X e^{-i k_{X2} r \hat{e}_X} e^{-i \omega_{X2} t} \right] \right\}$$

(18)

where we have assumed that the X-ray pulse $X2$ is in a coherent state with expectation value

$$\langle A_{X2}(r) A_{X2}^\dagger(t) \rangle = \langle \hat{\mathbf{A}}_{X2}(\omega_k - \omega_{X2}) e^{i k_{X2} r} e^{-i \omega_{X2} t} \rangle$$

given by the associated classical field.

The evolution of the current density $\langle \hat{j}^{(-)}(r, t) \rangle$ associated with the SFG diagram$^{55}$ in Figure 1b is obtained to second order in perturbation theory, including the interaction with the XUV pump and the first X-ray probe pulse:

$$\langle \hat{j}^{(-)}(r, t) \rangle_{\text{SFG}} = \langle \hat{j} \rangle \int dt_1 \int dt_2 \langle \hat{\mathbf{A}}_{X1}(t_1) e^{-i \omega_{X1} t_1} \rangle \times \langle \hat{\mathbf{A}}_{XUV}(t_2 - t_1 + T) e^{-i \omega_{XUV} (t_2 - t_1 + T)} \rangle \times \langle \hat{\mathbf{G}}(k_{X1}) \hat{\mathbf{G}}(k_{X2}) \hat{\mathbf{G}}(k_{X1}) \hat{\mathbf{G}}(k_{X2}) \rangle \times \langle \hat{j} \rangle$$

(19)
where we have defined the initial state of the system \( \hat{\rho}_0 = |g\rangle \langle g| \), the operator
\[
\hat{f}^{(+)}(k) = \int d^3r \hat{f}^{(+)}(r)e^{ikr}
\]
and the free-evolution operator \( \hat{G}(t) \) which also includes the decay rates of the system. By inserting eq 19 into eq 18, and after performing the integrals in \( t_f \) and \( t_2 \) explicitly assuming that the X-ray pulses do not overlap with the XUV pump pulse, we obtain the following sum-over-states expression for the signal:
\[
S(\alpha_f, T, k_{X1}, k_{X2}) = 2\text{Im} \left\{ \sum_{\ell_f} \mathcal{A}_{\alpha_f}^2(\alpha_f - \omega_{X2}) \times \mathcal{A}_{\alpha_f}(\alpha_f - \omega_{X1} + i\eta_f) \frac{e^{-i\omega_f T}e^{-\xi_f^2}}{-i(\alpha_f - \omega_f + i\eta_f)} \times \mathcal{A}_{X_{UV}}(\alpha_g - \omega_{X_{UV}} - i\eta_f) \times \hat{f}_{\alpha_f}(k_{X1}) \hat{f}_{\alpha_f}(k_{X2}) \hat{\xi}_{X_{UV}}(k_{X_{UV}}) \hat{\xi}_X(k_{X1}) \hat{\xi}_X(k_{X2}) \right\}
\]
(21)
Since the XUV pump-pulse wavelength is significantly shorter than the molecular size and the wavelength of the X-ray pulses X1 and X2, eq 21 reduces to eq 5.

# B. ESTIMATION OF THE SIGNAL-TO-BACKGROUND RATIO

The spectra in Figures 2 and 3 were displayed in arbitrary units. The signal-to-background ratio
\[
R(\alpha_f) = \frac{8\pi n_{\text{mol}} L S(\alpha_f)}{\mathcal{A}_{X_{UV}}^2 C X_{UV}^2 \omega_{X1} \omega_{X2} e^{-(\omega_f - \omega_{X1})^2 / \tau_{X1}^2}}
\]
(22)
can be estimated by comparing the number of absorbed photons \( N_{\text{abs}}(\alpha_f) \) to the number of probe-pulse photons \( \mathcal{A}_{\alpha_f} \omega_{X2} \delta \omega \) in the differential interval \( \delta \omega \), centered on \( \omega_f \). \( n_{\text{mol}} \) is the density of molecules in the focal area \( \mathcal{A}_{\alpha_f} \) and propagation length \( L \), the fine-structure constant, and
\[
\hat{I}(\alpha_f) = \frac{1}{8\pi \alpha} \mathcal{A}_{\alpha_f}(\alpha_f - \omega_{X2})^2 / 2\pi
\]
(23)
the pulse spectral intensity.

The signal-to-background ratio for the peak in Figure 3b due to the \( g \rightarrow e \rightarrow f \rightarrow g \) pathway. The associated transition current densities at fixed X-ray propagation directions are given by \( |\hat{f}_{\alpha_f}(k_{X1})|^2 \hat{\xi}_{X_{UV}}^2(\tau_{X_{UV}})^2 \hat{\xi}_X^2(\tau_{X1})^2 \), \( \hat{\xi}_X^2 = 0.44 \text{ au} \), and \( |\hat{f}_{\alpha_g}(k_{X_{UV}})|^2 \hat{\xi}_{X_{UV}}^2\hat{\xi}_X^2(\tau_{X_{UV}})^2 \), see also Figures 5 and 6. As predicted in Figure 4b, rotating the X-ray propagation direction in the \( xz \) plane causes a 10% change in the signal and in the signal-to-background ratio. We assume X-ray probe pulses with peak intensities \( |\mathcal{A}_{X_{UV}}|^2 \omega_{X_{UV}}^2 / (8\pi \alpha) = 1.5 \times 10^{18} \text{ W/cm}^2 \) and pulse durations \( \tau_{X_{UV}} = 100 \text{ as} \), and an XUV pump with \( |\mathcal{A}_{X_{UV}}|^2 \omega_{X_{UV}}^2 / (8\pi \alpha) = 3.1 \times 10^7 \text{ W/cm}^2 \) and \( \tau_{X_{UV}} = 200 \text{ as} \); these peak intensities can be reached experimentally and are associated with Rabi frequencies \( jA \) smaller than the associated line widths \( \gamma_1 \) and \( \gamma_2 \) ensuring the validity of the perturbative approach employed here. From eq 5, the signal strength at the peak frequency \( \omega_f = \omega_{Q2} \) can be estimated as
\[
S \approx 2/\gamma_f \sqrt{2\pi} \tau_{X_{UV}} \mathcal{A}_{X_{UV}}^2 \hat{f}_{\alpha_f}(k_{X1}) \hat{f}_{\alpha_f}(k_{X2}) \hat{\xi}_X(k_{X1}) \hat{\xi}_X(k_{X2}) \hat{\xi}_{X_{UV}}(k_{X_{UV}})
\]
(24)
For a molecule density \( n_{\text{mol}} = 1.6 \times 10^{15} / \text{cm}^3 \) and a short propagation length of \( L = 1 \text{ mm} \), eq 22 predicts a 0.27% signal-to-background ratio at the peak of the signal. Observing wavevector-dependent changes in this signal-to-background ratio is feasible, but may be challenging experimentally. Extended media can provide stronger signals, even though the detailed properties may be modified by propagation effects which were not accounted for here.

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### Notes

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