

pubs.acs.org/JACS

Time-Evolving Chirality Loss in Molecular Photodissociation Monitored by X-ray Circular Dichroism Spectroscopy

Yeonsig Nam,^{*,⊥} Daeheum Cho,^{*,⊥} Bing Gu, Jérémy R. Rouxel, Daniel Keefer, Niranjan Govind, and Shaul Mukamel^{*}

Cite This: J. Am. Chem. Soc. 2022, 144, 20400–20410			Read Online	
ACCESS	LIII Metrics & More		Article Recommendations	s Supporting Information

ABSTRACT: The ultrafast photoinduced chirality loss of 2-iodobutane is studied theoretically by time- and frequency-resolved X-ray circular dichroism (TRXCD) spectroscopy. Following an optical excitation, the iodine atom dissociates from the chiral center, which we capture by quantum non-adiabatic molecular dynamics simulations. At variable time delays after the pump, the resonant X-ray pulse selectively probes the iodine and carbon atom involved in the chiral dissociation through a selected core-to-valence transition. The TRXCD signal at the iodine L₁ edge accurately captures the timing of C–I photodissociation and thereby chirality loss, c.a 70 fs. The strong electric dipole–electric quadrupole (ED–EQ) response makes this signal particularly sensitive to vibronic coherence at the high X-ray regime. At the carbon K-edges, the signals monitor the molecular chirality of the 2-



butyl radical photoproduct and the spin state of the iodine atom. The ED-EQ response is masked under the strong electric dipolemagnetic dipole response, making this signal intuitive for the electronic population. The evolution of the core electronic states and its chiral sensitivity is discussed. Overall, the element-specific TRXCD signal provides a detailed picture of molecular dynamics and offers a unique sensitive window into the time-dependent chirality of molecules.

INTRODUCTION

Chirality is an important molecular property that governs many chemical and biological processes. The two enantiomers of a chiral molecule cannot be superimposed on their mirror images and interact differently with chiral receptors and with chiral light. Therefore, discerning and identifying enantiomers has become an important subject for controlling molecular chirality. The most mature techniques for chiral recognition rely on a small difference in the absorption of left and right circularly polarized light caused by a chiral molecule, known as circular dichroism (CD).¹ Hence, CD signals vanish for achiral molecules and racemic mixtures, providing valuable information about molecular conformations and enantiomeric excess of samples. A well-established time-resolved CD in an UV-vis regime maps the global chiral property of the molecule. It has been successfully applied to liquid systems to observe the formation or decay of chirality upon the structural change in the chiral center on the picosecond timescale.²

Time-resolved X-ray CD (TRXCD) is an extension of the corresponding optical technique that takes advantage of element(site)-specificity, ultrafast (to attosecond), and large bandwidth of X-ray pulses. The advent of X-ray free electron lasers (XFELs)^{3,4} and high harmonic generation (HHG)⁵ table top sources have opened new ways to measure electron and nuclear dynamics owing to their high temporal, spectral, and spatial resolutions. Theoretical spectroscopy has provided rationale and predictive models that bridge simulations and

experimental observations. For example, static X-ray CD signals at the chlorine $L_{2/3}$ -edge of chlorophenylethanols⁶ and TRXCD at the oxygen, nitrogen, and carbon K-edges in formamide⁷ were theoretically predicted. The latter is a small molecule, in which all cores are in close proximity to the chiral center; hence, the signals for the various K-edges are very similar and less distinguishable. Precise polarization control of X-rays at synchrotrons and FELs has been achieved recently, making chiral techniques available to a broader range of experiments. Extending the TRCD measurement into the X-ray regime, adds sensitivity to the local molecular chirality through an element-sensitive core-to-valence transition near the core-excited atom. Such signals are simpler to interpret than chiral HHG and photo-electron CD signals.

This study aims at monitoring the decay and evolution of molecular chirality during the photodissociation process at different frequency (element) window. We focus on 2iodobutane, which has a chiral center at the asymmetrically substituted C atom (marked with an *) adjacent to the iodine atom, as is illustrated in Figure 1a. A similar model, chiral 1-

Received: August 9, 2022 Published: October 27, 2022







Figure 1. (a) Pulse configuration for the time-resolved CD spectroscopy and molecular geometry of 2-iodobutane. The center of the mass of the 2butyl chain is placed in the *xy* plane, and the C–I bond is oriented along the *z*-direction The 20 fs UV pump ($\omega_{pu} = 4.8 \text{ eV}$) prepares the molecule in the excited state, attosecond left/right circularly polarized X-ray probe then detects the core-to-valence transition after the time delay *T*. (b–d) Adiabatic potential energy surface along the C–I bond distance. (b) Iodine 2s-edge core states, (c) carbon 1s edge core states (see the atomic labels in a). (d) valence electronic states. SC_n/TC_n labels in (b,c) refers to singlet/triplet core excited states, where *n* is ordered by increasing energies at the Frank–Condon geometry. A UV pump (E_{pu}) excites a molecule in the ground state into a valence manifold, then an X-ray probe (E_{pr}) tuned to either iodine 2s or carbon 1s edge excites again into a core state with a time delay *T*.

iodo-2-methylbutane was studied by Ilchen et al.⁸ to probe the ultrafast molecular fragmentation with photoelectron spectroscopy, thereby indirectly monitoring chirality loss. The photodissociation of methyl iodide (CH₃I), a prototypical model of alkyl halides, has been used for studying nonadiabatic dynamics and for developing new experimental techniques.^{9–12} The photoexcitation of the methyl iodide near-UV region (220-350 nm)¹⁰ by an optical pump pulse is known to mainly populate the ${}^{3}Q_{0}$ state in the A band, promoted by a nonbonding n electron of iodine to the lowest energy C–I antibonding σ^* molecular orbital. ($n \rightarrow \sigma^*$ transition). This weakens the C–I bond, resulting in a strongly dissociative character along the coordinate. Following excitation, the molecule undergoes nontrivial dynamics, including internal conversion and/or intersystem crossing facilitated by spin-orbit coupling, leading to the dissociation into a 2-butyl radical and an iodine atom as spin-orbit-excited $(I^*, {}^2P_{1/2})$ or

ground-state (I, ${}^{2}P_{3/2}$) with a finite energy gap.¹³ Substituting the hydrogen atoms of methyl iodide into heavier functional groups results in a different branching ratio as a photoproduct.¹⁴

Breakage of the C–I bond strongly modifies the molecular chirality. The CD measurements based on HHG spectroscopy demonstrated a strong chiroptical response of chiral 2-iodobutane during the ultrafast excitation, opposite in sign to that of the unexcited molecules, and the chiral signal persisted up to 250 fs and then decayed, corresponding to the formation of an achiral state for both products.¹⁵ The experimental technique is sensitive to the chiral evolution of the valence state projected onto the ground state of the cation. Thus, it is indirectly sensitive to nuclear dynamics with a not straightforward assignment of the electronic changes. The time-resolved photoelectron CD measurements of neutral 2-iodobutane from



Figure 2. Active space orbitals and the electronic transitions involved in the valence excited states (red, blue, and green lines), and the core excited states (black lines), at (a) short C–I distance (<3.37 Å) and (b) long C–I distance (>3.37 Å). Note that the ground states at the long C–I distance is described by the configuration state function where an electron in σ_2 is promoted to the σ^* molecular orbital.

the same group reported rapid decay within 60 fs, accounting for the rapid racemization of nascent 2-butyl radicals.¹⁶

The C atom at the chiral center site can be distinguishably probed due to their different binding energies, resulting from the de-screening induced by the adjacent iodine atom. As the iodine atom recedes from the adjacent carbon atom, the binding energy shifts of iodine L_1 and the carbon K edge change, which can act as an indicator of a chirality loss. Such element sensitivity of X-ray probes can provide a clear answer to whether the 2-butyl radical dissociates as a chiral or achiral product, and how the molecular chirality originating from the C–I bond and radical electron are different from each other.

We present a more complete set of spectroscopic signatures based on XFEL-based time- and frequency-resolved X-ray CD of the photodissociation of 2-iodobutane. We employ exact quantum nuclear wavepacket (WP) dynamics involving internal conversion and intersystem crossing on an equal footing, in reduced dimensionality. Earlier theoretical works had highlighted the importance of the electric quadrupoleelectric dipole (ED-EQ) response in anisotropic systems, where quadrupole transitions account for the pertinent inner shell excitations in natural CD in the X-ray region.^{17,18} The contribution of higher order multipoles (magnetic dipole, electric quadrupole, etc.) to the signals is much weaker than their nonchiral (electric dipole) counterparts by a factor a/λ , typically 10^{-2} to 10^{-3} , where *a* is the molecular size and λ is the incident light wavelength.¹⁹ This implies that for transition requiring a high X-ray regime, for example, iodine L1 edge, the magnitude of multipole becomes comparable to electric dipoles and one can achieve a larger asymmetry ratio in the X-ray (compared to the UV-vis) regime. We thus included the ED-EQ contribution to the XCD signal and the electric dipole-magnetic dipole (ED-MD) to provide more accurate descriptions of the chiral response.

We demonstrate the merits of the X-ray probe thanks to its characteristic elements and site specificity as well as strong electric quadrupole and magnetic dipole responses to the CD signal. We find that the iodine and carbon edges provide the different information about the molecular chirality, wherein the TRXCD signal at the iodine L_1 -edge (5230 eV) provides a highly localized probe of the chirality, giving a sensitive window into the timing of bond cleavage. The strong ED–EQ responses make this signal particularly sensitive to vibronic coherences. The carbon K-edge (270–290 eV) provides a window onto the energetic profile of core states, the chirality of the photoproduct 2-butyl radical, and the spin state of the iodine atom. The vibronic coherence contribution is masked by electronic populations in the dominating contribution from the ED–MD response.

RESULTS AND DISCUSSION

The potential energy surfaces (PESs) displayed in Figure 1d show the electronic energy of the valence electronic states along the reactive C-I coordinate. One-dimensional adiabatic PESs were computed by elongating/shrinking C-I internuclear distance from the optimized geometry at the Franck-Condon point as a reference, spanning from 1.7728 to 5.4228 Å by 512 grid points, without the geometry optimization of the remaining degrees of freedom. The complete active space selfconsistent field (CASSCF) level of theory consisting of 10 electrons in 11 orbitals and three valence states in the state averaging was implemented using the OpenMolcas software.²⁰ Three singlet and triplet core states were computed with ANO-RCC and cc-pVTZ basis sets for iodine 2s and carbon 1s core states, respectively. All quantities required for computing the X-ray signal are evaluated at 512 nuclear grid points and then extrapolated to 3072 grid points for nuclear WP dynamics simulation (see the Methods section for simulation details).

The first absorption band of alkyl halides consists of a broad band ranging from 220 to 350 nm, with a maximum at 260 nm,¹⁰ corresponding to a $n \rightarrow \sigma^*$ transition, where a nonbonding p electron of iodine is promoted to the lowest energy antibonding molecular orbital of the C–I bond. Owing to the presence of an iodine atom, a strong spin–orbit



Figure 3. Time-resolved electronic (a) populations, (b) coherences involving ground state, and (c) coherences involving only excited states.

coupling splits the transition into five electronic characters, labeled ${}^{3}Q_{2}$, ${}^{3}Q_{1}$ (green line), ${}^{3}Q_{0-}$, ${}^{3}Q_{0+}$ (blue line), and ${}^{1}Q_{1}$ (red) according to Mulliken's notation.^{21,22} Among these, only three spin-orbit states are accessible from the ground state, where the ${}^{3}Q_{1}$ and ${}^{1}Q_{1}$ states can be accessed with a perpendicular dipole transition, and are adiabatically correlated with the fragments in its ground spin–orbit state $I({}^{3}P_{3/2})$. The ${}^{3}Q_{0+}$ state can be accessed via a parallel transition and is correlated adiabatically with the spin-orbit excited state $I^*({}^{3}P_{1/2})$. The other ${}^{3}Q_2$ and ${}^{3}Q_{0-}$ states are dark and are often disregarded; thus, we mark the ${}^{3}Q_{0+}$ state as ${}^{3}Q_{0}$ for convenience. Our one-dimensional PES well describes the curve crossing between the singlet ${}^{1}Q_{1}$ and triplet ${}^{3}Q_{0}$ states occurring near the Franck-Condon point,⁸ as well as the energy gap between the photoproducts $I^*({}^2P_{1/2})$ and $I({}^2P_{3/2})$ with an energy gap of 0.87 eV, in agreement with the experiments.^{13,23} Thus, one can expect that the curve crossing facilitated by the small energy gap between the ${}^{1}Q_{1}$ and ${}^{3}Q_{1}$ complicates the molecular dynamics and makes it difficult to find the origin of photoproduct, whether it is produced adiabatically or nonadiabatically. We discuss the influence of other nuclear coordinates at the end of the section.

The carbon 1s core states are shown in Figure 1c. The carbon atom at the chiral center (C_1 , see the atomic labels in Figure 1a) can be distinguishably probed thanks to its different binding energies, resulting from the de-screening induced by the adjacent iodine atom. The core states above the C_1 1s edge are located energetically lower than those of the other carbon core states. Similarly, the other carbon atoms experience different levels of chemical shifts and are observed at different energy levels, where the C_2 1s edge core states are energetically higher than the C_3 and C_4 1s edges. The different chemical environments allow one to resolve the site-specific characteristics via a resonant X-ray probe.

Among the same carbon 1s edge, for example, above the C_1 1s edge, the three singlet and triplet core states are labeled SC_n and TC_n , respectively, where *n* is ordered by increasing the core state energies in the Franck–Condon geometry. Note that the same labeling of core state is applied to the iodine L_1 edge. We find that the lowest singlet core excited state, SC_1 , is involved in the transition C 1s $\rightarrow \sigma^*$, while the SC₂ and SC₃ have a double excitation character, where $n \rightarrow \sigma^*$ is also involved (Figure 2). The small energy splittings between SC_1 and TC_1 as well as between $SC_{2/3}$ and $TC_{2/3}$ are less distinguishable. A finite energy gap exists between the SC1 and the higher singlet core states, when the C-I bond is short. At longer C-I distances, over 3.37 Å, the coefficient of the configuration state function $[\sigma_2^1 n_1^2 n_2^2 (\sigma^*)^1]$ exceeds that of the ground configuration $[\sigma_2^2 n_1^2 n_2^2]$. Hence, the ground state is characterized by $\sigma_2 \rightarrow \sigma^*$, and the SC₁ exhibits double excitation characters. As the C–I bond dissociates, the σ_2 orbital, formed by a linear combination of C $2p_z$ and I $5p_{zy}$ experiences less atomic orbital overlap and obtains more atomic orbital-like characters. The I 5p_z becomes energetically similar to the other $n_{1/2}$ orbitals, which is mainly characterized by $5p_{x/y}$ atomic orbitals. Accordingly, one can expect that at an elongated C–I distance, SC₁ is energetically similar to SC_{2/3} as σ_2 becomes energetically similar to $n_{1/2}$. By the same argument, the electronic energies of all core states decrease over the C-I distance. We found that the spin-orbit coupling splits the core states of photoproducts, with a finite energy gap.

The iodine 2s core states are shown in Figure 1b. We find a larger energy splitting between SC_1 and $SC_{2/3}$. Because of the weak spin-orbit coupling between the core states, energy splitting of the core state at a long C–I distance, is not observed. If such splitting had existed, the large lifetime broadening of the iodine 2s edge, 1.53 eV, would have exceeded that of an energy gap of 0.87 eV, making it difficult to resolve it spectrally.

The time evolution of the 2-iodobutane is driven by the pump-pulse, which is simulated numerically by an exact solution of the time-dependent Schrodinger equation in a reduced one-dimensional PESs, including explicit laser excitation via dipole couplings between the electronic states. A UV pump with a 20 fs (0.1 eV) full width at half-maximum (fwhm) at a central frequency of 4.8 eV (258 nm) brings the molecule ${}^{3}Q_{0}$ excited-state selectively. A shorter circularly polarized attosecond X-ray pulse subsequently probes the molecule at variable time delays after the pump pulse. Approximately 40% of the ground state was depopulated and

pubs.acs.org/JACS

Article



Figure 4. Frequency- and time-resolved X-ray pump-probe signal at the iodine 2s edge for (a) dichroic signal (TRXCD, eq 6) and (b) absorption background (TRXAS, eq 7). The middle and the bottom panels on the LHS display the temporal traces of the total dichroic signal, at certain detection frequencies. Those at the RHS show the population (middle) and coherence (bottom) contributions to the non-chiral absorption signal, respectively. The incident X-ray probe tuned at $\omega_x = 5230$ eV, being resonant with the valence-to-core transition from valence to I(2s) core states. The full width half maximum bandwidth of the probe pulse is 20 eV. The TRXCD signal quickly decays within 70 fs because the excited nuclear WP reaches the dissociation limit.

excited to ${}^{3}Q_{0}$, with a minor population in the ${}^{3}Q_{1}$ state. This is in line with the experimental findings that the majority of the population is transferred to the ${}^{3}Q_{0}$ state via a parallel transition.²⁴ The nuclear WPs propagate from the Franck– Condon point following the gradient of the potential energy curves, leading to an increase of the C–I distance expectation value (Figure S2a). The populations in the electronic states exhibit pronounced oscillations due to the strong spin–orbit and nonadiabatic couplings being responsible for internal conversion and intersystem crossing, respectively (Figure 3). The populated singlet and triplet electronic states lie in a narrow energy window with spatially overlapping spin–orbit coupling and non-adiabatic coupling, making it non-trivial to separate between the two types of transitions.

We represent the time-evolving electronic population and the coherence magnitude as a function of the pump-probe time delay in Figure 3. The population shows that the excited nuclear WPs approach the dissociation limit, at around 4 Å within 70 fs because of the absence of barriers, and the population transfer thereafter is negligible. A major part of the excited state population returns to the ground state, facilitated by intersystem crossing and/or internal conversion, occurring at approximately 4 Å owing to their small energy splitting at long C-I distances. Accordingly, the ground-state population and the expected C-I distance slightly increased over time (Figure S2b), although most ground-state nuclear WP oscillates in the potential well. The minor part of the excited nuclear WP reaches the dissociation limit, yielding a photoproduct I*/I branching ratio of 1:3, which is slightly larger but similar to that of $i-C_3H_7I$ (1:2 ratio)²⁵ and much smaller than that of *tert*-butyl iodide (1:13 ratio).²⁶

The coherence magnitudes between the ground state and each excited state are the largest in the beginning, owing to the excitation by an optical pump, but decrease over the time as the overlap between the excited- and ground-state nuclear WP is reduced (Figure 3b). The finite magnitude after 70 fs originates from the intersystem crossing and internal conversion from the excited states to the ground state explained above. We found that the gradient of the ${}^{1}Q_{1}$ PES is larger than that of ${}^{3}Q_{0}$, which is quite similar to that of ${}^{3}Q_{1}$ (Figure 1d). This causes the ${}^{1}Q_{1}$ nuclear WP to pick up more kinetic energy than those in the other electronic states, leading to a smaller nuclear WP overlap with that of ${}^{3}Q_{1}$. In contrast, the ${}^{3}Q_{0}$ and ${}^{3}Q_{1}$ nuclear WP propagates similarly, maintaining a large nuclear WP overlap between those states, thereby larger coherence magnitude than that of ${}^{1}Q_{1}/{}^{3}Q_{0}$. We find that the internal conversion between triplet states is negligible because of their finite energy gap throughout the nuclear grids.

Next, we present the frequency- and time-resolved X-ray CD signals, represented by the loop diagram in Figure S1. We used a single broadband probe pulse (Figure 1, 20 eV bandwidth) and tuned its central frequency to the iodine L1-edge, at 5230 eV. The carbon atoms were probed by the field with a 15 eV bandwidth, and the central frequencies were tuned to 264, 279, 277, and 274 eV for C1 to C4 atoms, respectively. The signals were computed in the x-, y-, and z-polarization directions in the molecular frame and then rotationally averaged. In a pump-probe signal, the pump polarization breaks the sample isotropy, and it is necessary to rotationally average the signal over the entire optical process. In this case, two types of response tensors must be averaged: a four-rank tensor $\langle \mu\mu\mu m \rangle$ and a fifth-rank tensor $\langle \mu \mu \mu q \rangle$, as well as their permutations over the m and q interactions. This is to be contrasted with the standard static CD in which two-point matter correlation functions are averaged, $\langle \mu m \rangle$ and $\langle \mu q \rangle$. The latter tensor containing the quadrupolar contribution vanishes upon rotational averaging because the electric quadrupole is a symmetric tensor. In the pump-probe process, in contrast, $\langle \mu \mu \mu q \rangle$ survives the averaging and the electric quadrupole and then contributes to the signal. We consider the XXYY tensor element ($\varepsilon_x \varepsilon_x \varepsilon_y \varepsilon_x$ polarization of the electric field, where the last field propagates in the z-direction) for the electricmagnetic dipole interaction $\langle \mu\mu\mu m \rangle_{\Omega}$, and XXYZX tensor element for the electric dipole-quadrupole interaction $\langle \mu \mu \mu q \rangle_{\Omega}$ to have net scalar quantities for both interactions.

pubs.acs.org/JACS



Figure 5. TRXCD signals above (a) C_1 , (b) C_2 , (c) C_3 , and (d) C_4 K edge (see atomic label in Figure 1). The full width half maximum bandwidth of the probe pulse is 15 eV. The TRXCD signal survives even after 70 fs, due to the molecular chirality from the 2-butyl photoproduct. The upper or lower box in (b–e) indicates the TRXCD signal from the transition between valence excited states and $SC_{2/3}/TC_{2/3}$ or SC_1/TC_1 core excited states, respectively.

The TRXCD (eq 6) signal calculated at the iodine L_1 edge is displayed in Figure 4a. We first observe two strong peaks at 5226 and 5232 eV characterized by positive (red) and negative (blue) temporal oscillations (middle and bottom panels). These oscillations come from the superpositions of valence and/or ground states where the energy splittings between the states involved can be directly read from the oscillation period. CD is a weak signal relying on the small asymmetry of absorption between left and right circularly polarized light; thus, it is usually masked by the much stronger (around 2 orders of magnitude) non-chiral pump-probe (transient X-ray absorption, TRXAS) signals in the observations. However, in the high-frequency X-ray regime, the magnetic dipole and electric quadrupole magnitudes become comparable to electric dipoles, making it possible to achieve a larger asymmetry ratio than in the UV-vis regime. Indeed, we achieved 9.01% asymmetry ratio by dividing the maximum intensity of the TRXCD signal by that of the TRXAS signal for the leftpolarized probe, as shown in Figure 4b. Apart from the nonchiral component, the vibronic coherence information in TRXCD is usually masked by the stronger contribution from the ground state or excited populations. In iodine 2s edge, we note that $\mu^{\dagger}q - q^{\dagger}\mu$ term goes to 0 for populations (i = j), and only vibronic coherences $(i \neq j)$ contribute to the ED-EQ response according to eq 6. In contrast, the $\mu^{T}m-m^{T}\mu$ term

survives due to the imaginary component of transition magnetic dipole moment, and both population and coherence contribute to the ED-MD response. We compare the magnitude of ED-EQ, and ED-MD response at the iodine L_1 edge in Figure S3. We find that the ED-EQ response is 2 orders of magnitude larger than the ED-MD response, making the TRXCD signal particularly sensitive to the vibronic coherence. This makes the TRXCD signal useful not only for monitoring molecular chirality but also the electronic coherences emerging from the conical intersections.

The 5226 eV peak corresponds to the transition from the superposition of valence states to SC_1/TC_1 . This peak represents a pre-edge spectral window free from the ground-state background because a core electron is promoted to the semi-vacant n_1 or n_2 orbitals, where one electron is excited to σ^* in valence excited states (Figure 2). As occupied valence orbitals have lower energies than the virtual ones, the transient signals are expected to be red-shifted by several eV in the background-free pre-edge region. This makes the asymmetry ratio at the region stronger ca. 11.06%, when dividing the largest intensity of TRXCD (2.161 × 10⁻⁶) by that of TRXAS (1.954 × 10⁻⁵). The ground-state WP indirectly contributes to the signal through its superposition with excited states at early time delays, when the nuclear WPs are localized near the Franck–Condon point, and the nuclear WP overlap is finite.

Otherwise, the ground state can be populated by intersystem crossing or internal conversion at elongated C–I, where the electronic states are closely spaced. The TRXCD signal contributed by the $S_0/{}^3Q_1$ coherence to SC₁ and by the $S_0/{}^1Q_1$ coherence to TC₁ are observed at around 40–60 fs (Figure S4a).

We found that the signal at 5226 eV is particularly strong between 20 and 60 fs, when the intersystem crossings from ${}^{3}Q_{0}$ \rightarrow ¹Q₁ and the following ¹Q₁ \rightarrow ³Q₀ occur (Figure S4). This is evidenced by the fact that the signal involving ${}^{1}Q_{1}/{}^{3}Q_{0}$ coherence is strong between 20 and 40 fs, while ${}^1\vec{Q_1}/{}^3\vec{Q_1}$ coherence between 40 and 60 fs. Also, the PESs depicted in Figure 1d show that the crossing between ${}^{3}Q_{0}$ and ${}^{1}Q_{1}$ occurs near the Franck–Condon point, and then the ${}^{1}Q_{1}$ approaches that of ${}^{3}Q_{1}$ as the C-I bond is elongated. The internal conversion between ${}^{3}Q_{0}$ and ${}^{3}Q_{1}$ may not be efficient because of their finite energy gap. Both coherences exhibit characteristic oscillations with different periods, making the pattern complicated. Distinguishing the contributions of different coherences to the TRXCD signal help resolve the timing of the passage through conical intersections between electronic states.

The 5232 eV peak is related to the transitions from the excited states to $SC_{2/3}$ and from the ground state to SC_1/TC_1 , whereas the transitions to the higher triplet states, $TC_{2/3}$ are negligible. Because the same orbital transitions are involved, the asymmetry ratio in this region is weaker than in the preedge region ca. 7.51%, when dividing the largest intensity of TRXCD (1.855 \times 10⁻⁶) by that of TRXAS (2.470 \times 10⁻⁵). The most prominent features at this region are the peak is observed from -10 fs when the optical pump populates the excited states and the superposition of excited states and the ground state is created (Figure S4c,d). The transition to SC_2 is strong between -10 and 30 fs, whereas that to SC₃ is strong between 40 and 60 fs. Note that the pump populates both ${}^{3}Q_{1}$ and ${}^{3}Q_{0}$ states, which allows one to observe their coherence in the TRXCD signal. The signal survives until the C-I bond breaks up and the molecule loses its chirality due to their similar PES gradients and their finite nuclear WP overlaps not by the internal conversion, which is prevented by their finite energy gap over the numerical grids.

We find that both 5226 and 5232 eV peaks decay after 70 fs, which is in agreement with the recent studies of Wörner et al.,¹⁶ giving a sensitive window for the chirality loss of 2iodobutane upon C-I dissociation. In contrast, the non-chiral TRXAS signal (Figure 4b) survives even after the C-I dissociation. The two peaks at 5226 and 5232 eV do not show oscillatory features but just decrease over time as the population of the excited state decreases. We find that after C-I dissociation, the signal is facilitated by inner shell excitation, iodine $2s \rightarrow 5p$ transition. The transition from the ground state constitutes a negative background, located mainly at 5230 eV, involving the SC_1/TC_1 core states, and partially overlaps with the peak at 5232 eV. The period of this peak is 70 fs (476 cm⁻¹), corresponding to a C–I vibration of 500-600 cm⁻¹. The ground-state WP oscillates in the reactive coordinate within the dissociation limit, while the excited-state WP passes by the region, where the C–I distance is elongated, and the iodine atom is no longer involved in the molecular chirality. This causes the TRXCD signal to vanish after 70 fs, whereas the TRXAS signal is maintained.

population (middle panel); hence, it is somewhat masked in the total signal (top panel). By contrast, the vibronic coherence term is directly accessible in the TRXCD signal at the iodine L_1 edge. Note, however, that they provide intrinsically different information, where the coherence term in the non-chiral signal is characterized by the ED–ED term, whereas that in TRXCD is characterized by ED–MD and ED–EQ.

We now turn to the TRXCD signals at the carbon K-edges, as displayed in Figure 5. We first note that the signals are mostly contributed by the population, whereas coherence contributions are masked. This is because the magnitude of ED-MD response, where population masks coherence contribution (Figure S5), is at least an order of magnitude stronger than that of the ED-EQ response, in contrast to iodine L_1 edges. Due to the large ground-state population, which masks time-evolving molecular chirality, Figure 5 plots the differential signal, after subtracting the static XCD signal calculated in the absence of pump interaction.

The TRXCD signal for C_1 1s edges (Figure 5b) shows two positive peaks at around 260.3 eV involving the lowest core states $(SC_1 \text{ and } TC_1)$ and at around 263 eV involving higher core excited states (SC_{2/3} and TC_{2/3}) from valence excited states. The latter is partially canceled out by the negative peak observed at around 264-267 eV, arising from the transitions between the ground state and core excited states. We find that the spectroscopic signature does not vanish even after 70 fs, due to the chirality of the 2-butyl radical. Both positive absorption lines converge mostly to 260.3 eV as the C-I bond dissociates and the energy gap between the core states vanishes. Note that the peak at 260.3 eV is also contributed by the ground state, which is populated by internal conversion from ${}^{1}Q_{1}$ and intersystem crossing from ${}^{3}Q_{1}$ at elongated C–I distances. The transition from the ${}^{3}Q_{0}$ state is detected at the lower window (259.5 eV), as shown in Figure S6a. This is because the I* spin excited state, which is adiabatically coordinated by the ${}^{3}Q_{0}$ valence state, is energetically higher than the spin ground-state I by 0.8 eV, coordinated by the ground-state, ${}^{3}Q_{1}$, and ${}^{1}Q_{1}$ states (Figure 1d). This peak is hidden in Figure 5b due to its small population.

We separately plot the TRXCD signal above C_1 1s edges, contributed by the vibronic coherence at Figure S6b for comparison. We note that the coherence contribution is 2 orders of magnitude smaller than the population contribution. Similar to Figure 5b, the signal begins with a broad nature and converges to two peaks at 259.5 and 260.3 eV but with more complicated patterns, due to the phase oscillation. The peak at 259.5 eV, contributed from ${}^{3}Q_{0}$, is relatively well observed with a characteristic oscillation of 5.17 fs, corresponding to an energy gap of 0.8 eV, due to the large enough ${}^{3}Q_{0}/{}^{3}Q_{1}$ vibronic coherence compared to others (Figure 3b,c). Meanwhile, the higher window (at 260.3 eV), originating from the coherence involving ${}^{3}Q_{1}$, ${}^{1}Q_{1}$, and the ground state, constitutes a constant negative absorptive character because of their negligible energy splittings. If one can extract the TRXCD signal contributed by specific coherence contributions from the total signal, one can get further insights about the vibronic coherences.

 C_2 and C_3 atoms are located next to the chiral center and experience similar chemical changes, where their chemical shifts differ by 2 eV. An interesting feature is that the transition energies between the valence manifold and the lowest core excited states, SC_1 and TC_1 , increase along the C–I reactive coordinates. Specifically, the TRXCD signal above the C_2 1s edge began at approximately 276.5 eV (lower box) and approached 279.3 eV after C–I dissociation (Figure S5b, top and the bottom panels). This feature becomes dark as the C–I elongates and the orbital overlap between C 1s and I $n_{1/2}$ vanishes. In contrast, the transition energies between the valence excited states and the higher core states, SC_{2/3} and TC_{2/3} begins at around 282 eV (upper box) and then decreases to 279.3 and 278.5 eV. It is well recorded in the TRXCD signal, facilitated by C 1s to C $2p_z$ transitions even at elongated C–I bonds. We find the overlap of this positive peak and negative ground-state background in the beginning because the same C 1s $\rightarrow \sigma^*$ transition is involved.

One can attribute the increasing $(SC_1 \text{ and } TC_1)$ or decreasing $(SC_{2/3}/TC_{2/3})$ trends to the different gradients of the electronic surfaces. Specifically, we find that the slopes of the lowest core excited states, SC_1 and TC_1 , are smaller than those of the valence excited states. The electronic energies of the valence states decreases faster, increasing the transition energy over the C-I distance. Higher core excited states exhibited a slower decrease in energy, leading to a decreasing trend in the transition energies over the nuclear grid. For the iodine 2s edge, we did not observe a noticeable frequency change in the absorptive lines within the detection frequency window (Figure 4a). We find that the gradient of PESs for the iodine 2s edge is relatively similar to that of the valence excited states along the C-I reactive coordinate. While the carbon edges showed more dramatic changes in the energy profile over the reactive coordinate, giving more sensitivity to the evolution of the transition energies. The evolution of the valence electronic states can be directly accessible by X-ray photoelectron spectroscopy, while the evolution of the core excited state is accessible by resonant X-ray probes with element and site specificity.

A similar argument can be applied to the C_3 1s edge. Note, however, that the TRXCD signals of C_2 and C_3 1s edges somewhat overlap at around 276.5 eV (Figure 5a). Both C_2 and C_3 atoms are located left/right of the chiral center (C_1 atom) and thus experience similar chemical changes upon C–I dissociation. We find the similarities in their evolution of PESs and strong sensitivity to the TC₁ state compared to other core states. Using a resonant X-ray probe enables the monitoring of such chemical similarities. The core excited states above the C_4 1s edge exhibit three distinctive energy levels at 272.43, 273.16, and 273.65 eV. Thanks to the sufficiently narrow lifetime broadening of the carbon 1s edge, they can be distinguished spectrally in the X-ray signals, especially by the complicated negative peak of the ground-state background.

In all carbon 1s edges, we find the clear signature of energy evolution of valence-to-core transitions and molecular chirality originating from photoproduct 2-butyl radicals. Note that our effective Hamiltonian contains a single nuclear degree of freedom. The out-of-plane bending of the CHO group is responsible for the positive/negative oscillatory pattern with a 120 fs period in our previous work on formamide.⁷ Similarly, the 2-butyl radical racemization, induced by a 60 fs umbrella mode, was observed recently.¹⁶ We thus expect that the inclusion of out-of-plane mode will make the observed TRXCD signals decay by the time with positive/negative oscillations.

The pump pulse can further induce rotational excitation that may be responsible for rotational dephasing of CD signals. Worner et al.¹⁵ reported that for typical expected rotational temperatures of 5-30 K, the rotational anisotropy decays on a 11 to 5 ps time scale. This is much longer than the observed

decay in CD signals in tens of femtosecond time scale; hence, one can exclude rotational dynamics as the origin of the femtosecond decay of the signal observed in experiments. In another work of Moromukam et al.,²⁷ the rotational excitation is hot when nuclear WP arrives at the conical intersection, after some elongation of the C-I bond. If a rotational transition is made onto the ${}^{1}Q_{1}$ surface to give an I-channel product, which is flat with respect to the bending angle, it retains the rotational excitation, whereas a large bending force constants interrupts the rotational excitation in the I* channel coordinated by the ${}^{3}Q_{0}$ surface, preferring a bent CH₃ (chiral) conformation until the CH₃-I distance becomes very large. It implies that the TRXCD signal involving the ${}^{1}Q_{1}$ channel will decay faster than the ${}^{3}Q_{0}$ channel. Along with the different transition energies between I* and I channels, this fact could be used to distinguish two different dissociation channels.

Multiconfigurational time-dependent Hartree algorithm, involving five active vibrational modes (umbrella vibration, symmetric C–H stretching vibration, perpendicular rotation, and parallel rotation) has been used to present A-band photodissociation dynamics of methyl iodide on three relevant excited ab initio PESs to represent the experimentally observed dynamical activity.²⁸ Inclusion of the other nuclear degree of freedoms will provide a complete set of the TRXCD signal but it is beyond the scope of the article and we leave them as our future work.

CONCLUSIONS

The photodissociation of 2-iodobutane was studied by simulating time-resolved X-ray CD spectroscopy, combined with an exact quantum nuclear WP dynamics involving nonadiabatic transitions and spin-orbit interactions. The probe pulse was tuned to either the iodine L1 edge or the carbon K edge, providing an element-sensitive picture of chirality loss upon C-I photodissociation. The frequency- and time-resolved TRXCD signals provide clear signatures of the loss of molecular chirality upon photodissociation of the C-I bond within 70 fs. The spectral resolution of the TRXCD signal allows for different local windows on the molecular chirality by selecting a specific core-to-valence transition by tuning the frequency of the incident X-ray probe. X-ray chiral spectroscopy is more sensitive to molecular chirality because the rotatory strengths involved in the transitions are more localized around the equilibrium geometry than those involved in the valence-to-valence transitions. We demonstrated that probing the iodine edge monitors the loss of molecular chirality upon C-I photodissociation within 70 fs, which is in line with experiments. The strong ED-EQ response makes the signal sensitive only to vibronic coherence. This makes it possible to infer conical intersection passages in non-adiabatic dynamics. In contrast, the carbon edges allow monitoring of the evolution of the core states, molecular chirality of the 2butyl photoproduct, and the spin state of the dissociated iodine atom. The vibronic coherence information is masked by the population due to the stronger ED-MD response than ED-EQ. The realization of TRXCD would provide a powerful source for detecting ultrafast changes in the molecular chirality upon photochemical reactions.

METHODS

Frequency- and Time-Resolved X-ray CD Signal. The TRXCD signal is defined as the difference between the absorption spectra of the left and right circularly polarized probes following

$$H = H_0 + H_{\rm pr}(t) \tag{1}$$

where H_0 (eq 10) represents the Hamiltonian of a free molecule upon optical excitation propagated under the nonadiabatic and spin–orbit couplings and

$$H_{\rm pr}(t) = -\boldsymbol{\mu} \cdot \boldsymbol{E}_{\rm pr}(t) - \boldsymbol{m} \cdot \boldsymbol{B}_{\rm pr}(t) - \boldsymbol{q} \cdot \nabla \boldsymbol{E}_{\rm pr}(t)$$
(2)

represents the interaction with the probe and is treated perturbatively. Here, μ and m are the electric and magnetic dipoles, respectively, and q is the electric quadrupole moments. E and B are the electric and magnetic fields, respectively.

The signal is measured at the spectrally dispersed frequency ω and variable optical pump-X-ray probe time delay *T*. The time- and frequency-resolved absorption of a weak probe $A^{L/R}$ is given by^{29,30}

$$\boldsymbol{A}^{L/R}(\omega, T) = 2\omega \operatorname{Im}[\boldsymbol{E}_{\mathrm{pr}}^{L/R*}(\omega) \cdot \boldsymbol{P}^{L/R}(\omega, T) + \boldsymbol{B}_{\mathrm{pr}}^{L/R*}(\omega) \cdot \boldsymbol{M}^{L/R}(\omega, T) + \nabla \boldsymbol{E}_{\mathrm{pr}}^{L/R*}(\omega) \cdot \boldsymbol{q}^{L/R}(\omega, T)]$$
(3)

where $P^{L/R}(\omega, T)$ and $M^{L/R}(\omega, T)$ are the ω Fourier components of the polarization and magnetization, respectively. The superscript L/R indicates the left or right polarization of the electric and the magnetic fields. The time- and frequency-resolved TRXCD signals are given by the difference between the absorptions of the left- and right-polarized probes.

$$S_{\text{TRXCD}} = 2\omega \text{Im}[\boldsymbol{E}_{\text{pr}}^{\text{L}}(\omega) \cdot \boldsymbol{P}^{\text{L}}(\omega, T) + \boldsymbol{B}_{\text{pr}}^{\text{L}}(\omega) \cdot \boldsymbol{M}^{\text{L}}(\omega, T) - \boldsymbol{E}_{\text{pr}}^{\text{R}*}(\omega) \cdot \boldsymbol{P}^{\text{R}}(\omega, T) - \boldsymbol{B}_{\text{pr}}^{\text{R}*}(\omega) \cdot \boldsymbol{M}^{\text{R}}(\omega, T) + \nabla \boldsymbol{E}_{\text{pr}}^{\text{L}}(\omega) \cdot \boldsymbol{q}^{\text{L}}(\omega, T) - \nabla \boldsymbol{E}_{\text{pr}}^{\text{R}}(\omega) \cdot \boldsymbol{q}^{\text{R}}(\omega, T)]$$
(4)

The signal vanishes in the dipole approximation and only the pseudoscalar quantity of the signal, which contains one interaction with the electric dipole and one with the magnetic dipole or electric quadrupole, survives. The interaction with the X-ray probe is calculated perturbatively in $H_{\rm pr}(t)$. Expanding the polarization in eq 4 to the first order in the probe field and using the basis $|\varphi_i(\mathbf{r}, \mathbf{R})\rangle$ of the adiabatic electronic state (abbreviated as $|i\rangle$ below) leads to

$$S_{\text{TRXCD}} = 4\omega \text{Im} \int_{-\infty}^{\infty} dt \ e^{-i(\omega - \omega_c)t} \int_{0}^{t} dt_1$$

$$\sum_{ij} c_i(t_1) c_j^*(t) \langle \chi_j(t) | \chi_i(t_1) \rangle [\boldsymbol{\mu}_{jc}^{\dagger}(t) \boldsymbol{m}_{ci}(t_1) - \boldsymbol{m}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1)$$

$$+ i\omega (\boldsymbol{\mu}_{jc}^{\dagger}(t) \boldsymbol{q}_{ci}(t_1) - \boldsymbol{q}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1))] a_{\text{pr}}(\omega) a_{\text{pr}}(t_1 - T)$$

$$e^{-i(\omega_c - \omega_{\text{pr}})t_1}$$
(5)

Here, $|\Psi(\mathbf{r}, \mathbf{R}, t)\rangle$ represents the free evolution of the system following the pump pulse $|\Psi(\mathbf{r}, \mathbf{R}, t)\rangle = \sum_{i} c_i(t) |\chi_i(\mathbf{R}, t)\rangle |\varphi_i(\mathbf{r}, \mathbf{R})\rangle$, where $\chi_i(\mathbf{R}, t)$ is the time-dependent normalized nuclear WP on the valence PES *i*, with the amplitude of the adiabatic surface $c_i(t)$. t_1 is the time duration between interactions (the time duration in the core states) and *c* is the speed of light.

In the impulsive limit, where $a(t_1 - T) = \delta(T)a$ and $t_1 \rightarrow 0$, the Fourier transform of the probe pulse to the frequency domain yields the final signal

$$S_{\text{TRXCD}}(\omega_s, T) = -4\omega \operatorname{Rea}(\omega_s) a^*(\omega_s) \sum_{ijc} c_i(T) c_j^*(T) \langle \chi_j(T) | \chi_i(T) \rangle$$

$$\times [\{\boldsymbol{\mu}_{jc}^{\dagger}(T) \boldsymbol{m}_{ci}(T) - \boldsymbol{m}_{jc}^{\dagger}(T) \boldsymbol{\mu}_{ci}(T) + i\omega_s [\boldsymbol{\mu}_{jc}^{\dagger}(T) \boldsymbol{q}_{ci}(T) - \boldsymbol{q}_{jc}^{\dagger}(T) \boldsymbol{\mu}_{ci}(T)]\}$$

$$/\{\omega_s - \omega_{ci} + i\Gamma_c\}]$$
(6)

We introduce the lifetime broadening of 0.100 eV (for the C 1s edge) and 1.53 eV (I 2s edge) for Γ_c^{31} As a reference, we present the non-chiral pump–probe signal (transient X-ray absorption, TRXAS), calculated by considering only the electric–electric contribution

$$S_{\text{TRXAS}}(\omega_s, T) = -4\omega \text{Im}a(\omega_s)a^*(\omega_s)$$

$$\sum_{ijc} \frac{c_i(T)c_j^*(T)\langle \chi_j(T)|\chi_i(T)\rangle \boldsymbol{\mu}_{jc}^{\dagger}(T)\boldsymbol{\mu}_{ci}(T)}{\omega_{\rm s}-\omega_{\rm ci}+i\Gamma_{\rm c}}$$
(7)

ELECTRONIC STRUCTURE SIMULATIONS

The electronic structure of the valence manifold was obtained at the state-average CASSCF level.³² The active space consists of 10 electrons in 11 orbitals, including C-I $\sigma^{(*)}$ (anti)bonding orbitals and iodine lone pairs, *n* orbitals. Three states, the ground state, S_1 , and S_2 , were included in the state averaging. The core hole states were calculated in separate RASSCF calculations³³ by freezing the optimization of the 2s orbital of the I atom or 1s orbitals of the C atoms, rotating them into the active space, and restricting their occupation to a single electron. For iodine 2s core states, scalar relativistic effects were included via a second-order Douglass-Kroll-Hess Hamiltonian in combination with an ANO-RCC basis set,^{34,35} with valence double zeta contractions. For the carbon 1s core states, the cc-pVTZ basis sets³⁶ were used without relativistic effects. All quantum calculations were implemented using OpenMolcas software.²⁰ The three triplet valence and core states were computed similarly by state averaging. Then, the quantities, such as transition electric/magnetic dipole moments, electric quadrupole moments, nonadiabatic coupling between the same spin states, and spin-orbit coupling between different multiplicities were computed via the RASSI module.³

NONADIABATIC NUCLEAR WP DYNAMICS

The time evolution of 2-iodobutane driven by the pump pulse was simulated numerically by an exact solution of the timedependent Schrödinger equation in spin-diabatic PESs, which depends on the energetic order of the adiabatic PESs within the same spin multiplicities. The molecular geometry of the ground state is optimized at the SA-3-CAS(10/11) level and used to construct one-dimensional nuclear degrees of freedom describing the C–I stretching spanning from 1.7728 to 5.4228 Å by 512 grids for our effective Hamiltonian. The equilibrium geometry at the ground-state minimum corresponds to 2.3228 Å, which is in line with previous studies.³⁸ All quantities, including the PESs, non-adiabatic coupling between the same spin states, spin-orbit couplings between the different multiplicities, and other quantities required for computing the X-ray signal, such as transition electric, magnetic dipole moment, and electric quadrupole moments are evaluated by scanning the 512 nuclear grid points, and then extrapolated to 3072 grid points. The PESs were computed along the "frozen" dissociation path, where the C-I distance increased over the grids, and the other atoms were kept fixed at the equilibrium geometry by receding iodine atom from the 2-butyl radical. The extrapolated quantities were approximated to be the same as those at the 5.4228 Å (512nd grid). The nuclear dynamics were launched by using a 20 fs fwhm Gaussian laser pump in resonance with the $S_0 \rightarrow {}^{3}Q_0$ transition, as was done in Worner's paper¹⁵

$$\boldsymbol{E}_{\rm pu}(t) = a_{\rm pu}(t)\boldsymbol{e}_{\rm L/R}\sin(\omega_{\rm pu}\cdot t), \ a_{\rm pu}(t) = a_{\rm 0} {\rm e}^{-t^2/2\sigma_{\rm pu}^2} \qquad (8)$$

The 1.52×10^{-3} a.u. of the electric field amplitude (a_0) and $\omega_{pu} = 4.8$ eV, the central frequency was used to excite a molecule in the ground state to excited state manifolds. The

$$i\hbar\frac{\partial}{\partial t}\begin{bmatrix}\chi_{1}(t)\\\vdots\\\chi_{n}(t)\end{bmatrix} = \begin{bmatrix}\mathbf{H}_{11} & \dots & \mathbf{H}_{1n}\\\vdots & \ddots & \vdots\\\mathbf{H}_{n1} & \dots & \mathbf{H}_{nn}\end{bmatrix}\begin{bmatrix}\chi_{1}(t)\\\vdots\\\chi_{n}(t)\end{bmatrix}$$
(9)

where the entries on the diagonal of the Hamiltonian matrix describe the uncoupled adiabatic dynamics of individual PESs

$$H_{ii} = T + V_{ii}(R)$$

$$H_{ij} = V_{\text{NAC}} + V_{\text{SOC}} - \mu E_{\text{pu}}(t)$$
(10)

with the pre-calculated PES $V_{ii}(R)$ of state *i* and nuclear kinetic energy operator $T = \frac{\hbar^2}{2m} \nabla^2$. The coupling between the different electronic states is described by the off-diagonal elements (H_{ij}) , which contains the interaction with the laser light $(\mu E_{pu}(t))$, nonadiabatic (V_{NAC}) , and spin—orbit coupling (V_{SOC}) . The WP is propagated by a Runge—Kutta fourth-order propagation scheme with a 0.05 fs time step until a final time of 162 fs. The operation of the nuclear kinetic energy operator on the nuclear WPs is performed using a fast Fourier transform. The grid, extending to 23.7085 Å, is large enough to prevent the nuclear WP from reaching the right boundary and thus can be alternatively used instead of absorbing the part of the WP at the end. The nuclear WP reaches approximately 12.6228 Å at 162 fs.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08458.

Derivation of the signal, loop diagram rule, rotational averaging, and supplementary figures: expected C–I distance over time, and TRXCD signal dissected into core and valence states, electric dipole-electric quadrupole, or magnetic dipole response (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Yeonsig Nam Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States; orcid.org/0000-0003-0386-9118; Email: yeonsign@ uci.edu
- Daeheum Cho Departments of Chemistry, Kyungpook National University, Daegu 41566, South Korea; orcid.org/0000-0002-0322-4291; Email: daeheumc@knu.ac.kr
- Shaul Mukamel Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States; orcid.org/0000-0002-6015-3135; Email: smukamel@ uci.edu

Authors

- Bing Gu Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States; Occid.org/ 0000-0002-5787-3334
- Jérémy R. Rouxel UJM-Saint-Étienne, CNRS, Graduate School Optics Institute, Laboratoire Hubert Curien UMR

5516, University Lyon, Saint-Etienne 42023, France; orcid.org/0000-0003-3438-6370

- Daniel Keefer Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States; orcid.org/0000-0001-5941-5567
- Niranjan Govind Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, United States; © orcid.org/ 0000-0003-3625-366X

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.2c08458

Author Contributions

 $^{\perp}$ Y.N. and D.C. contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The support of the Chemical Sciences, Geosciences, and Biosciences division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy through award no. DE-FG02-04ER15571 (S.M.) and KC-030103172684 (N.G.) and of the National Science Foundation (grant no. CHE-1953045) is gratefully acknowledged. We greatly appreciate Artur Nenov for fruitful discussion for implementing quantum calculations. D.C. was supported by the National Research Foundation of Korea (NRF) grant, funded by the Korea government (MSIT) (no. 2021R1C1C2007977) and J.R.R. was supported by the LabEx MANUTECH-SISE (ANR-10-LABX-0075) of the Université de Lyon, within the program "Investissements d'Avenir" (ANR-11-IDEX-0007). D.K. gratefully acknowledges support from the Alexander von Humboldt Foundation through the Feodor Lynen program. This research used resources of the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract no. DE-AC02-05CH11231, and National Supercomputing Center (South Korea) with resources including the technical support (KSC-2022-CRE-0160). A portion of the research was performed using EMSL, a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle Memorial Institute for the United States Department of Energy under DOE Contract no. DE-AC05-76RL1830.

REFERENCES

(1) Berova, N.; Nakanishi, K.; Woody, R. W.Circular Dichroism: Principles and Applications, 2nd ed.; Wiley, 2000.

(2) Oppermann, M.; Bauer, B.; Rossi, T.; Zinna, F.; Helbing, J.; Lacour, J.; Chergui, M. Ultrafast broadband circular dichroism in the deep ultraviolet. *Optica* **2019**, *6*, 56–60.

(3) Ding, Y.; Huang, Z.; Ratner, D.; Bucksbaum, P.; Merdji, H. Generation of attosecond x-ray pulses with a multicycle two-color enhanced self-amplified spontaneous emission scheme. *Phys. Rev. Spec. Top. Accel. Beams* **2009**, *12*, 060703.

(4) Schneidmiller, E. A.; Yurkov, M. V. Obtaining high degree of circular polarization at x-ray free electron lasers via a reverse undulator taper. *Phys. Rev. Spec. Top. Accel. Beams* **2013**, *16*, 110702.

(5) Novotny, L.; van Hulst, N. Antennas for light. *Nat. Photonics* **2011**, *5*, 83–90.

(6) Zhang, Y.; Rouxel, J. R.; Autschbach, J.; Govind, N.; Mukamel, S. X-ray circular dichroism signals: a unique probe of local molecular chirality. *Chem. Sci.* **2017**, *8*, 5969–5978.

(7) Rouxel, J. R.; Kowalewski, M.; Mukamel, S. Photoinduced molecular chirality probed by ultrafast resonant X-ray spectroscopy. *Struct. Dyn.* **2017**, *4*, 044006.

(8) Allum, F.; et al. A localized view on molecular dissociation via electron-ion partial covariance. *Commun. Chem.* **2022**, *5*, 42.

(9) Allum, F.; et al. Coulomb explosion imaging of CH3I and CH2ClI photodissociation dynamics. *J. Chem. Phys.* 2018, 149, 204313.

(10) Rubio-Lago, L.; García-Vela, A.; Arregui, A.; Amaral, G. A.; Bañares, L. The photodissociation of CH3I in the red edge of the A-band: Comparison between slice imaging experiments and multisurface wave packet calculations. *J. Chem. Phys.* **2009**, *131*, 174309.

(11) Gardiner, S. H.; Lipciuc, M. L.; Karsili, T. N. V.; Ashfold, M. N. R.; Vallance, C. Dynamics of the A-band ultraviolet photodissociation of methyl iodide and ethyl iodide via velocity-map imaging with 'universal' detection. *Phys. Chem. Chem. Phys.* **2015**, *17*, 4096–4106.

(12) Attar, A. R.; Bhattacherjee, A.; Leone, S. R. Direct Observation of the Transition-State Region in the Photodissociation of CH3I by Femtosecond Extreme Ultraviolet Transient Absorption Spectroscopy. J. Phys. Chem. Lett. 2015, 6, 5072–5077 PMID: 26636176.

(13) Eppink, A. T. J. B.; Parker, D. H. Methyl iodide A-band decomposition study by photofragment velocity imaging. *J. Chem. Phys.* **1998**, *109*, 4758–4767.

(14) Timmers, H.; Zhu, X.; Li, Z.; Kobayashi, Y.; Sabbar, M.; Hollstein, M.; Reduzzi, M.; Martínez, T. J.; Neumark, D. M.; Leone, S. R. Disentangling conical intersection and coherent molecular dynamics in methyl bromide with attosecond transient absorption spectroscopy. *Nat. Commun.* **2019**, *10*, 3133.

(15) Baykusheva, D.; Zindel, D.; Svoboda, V.; Bommeli, E.; Ochsner, M.; Tehlar, A.; Wörner, H. J. Real-time probing of chirality during a chemical reaction. *Proc. Natl. Acad. Sci. U.S.A.* **2019**, *116*, 23923–23929.

(16) Svoboda, V.; Ram, N. B.; Baykusheva, D.; Zindel, D.; Waters, M. D. J.; Spenger, B.; Ochsner, M.; Herburger, H.; Stohner, J.; Wörner, H. J. Femtosecond photoelectron circular dichroism of chemical reactions. *Sci. Adv.* **2022**, *8*, No. eabq2811.

(17) Carra, P.; Benoist, R. X-ray natural circular dichroism. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2000**, *62*, R7703–R7706.

(18) Peacock, R. D.; Stewart, B. Natural Circular Dichroism in X-ray Spectroscopy. J. Phys. Chem. B 2001, 105, 351–360.

(19) Tanaka, S.; Chernyak, V.; Mukamel, S. Time-resolved x-ray spectroscopies: Nonlinear response functions and Liouville-space pathways. *Phys. Rev. A: At., Mol., Opt. Phys.* **2001**, *63*, 063405.

(20) Fdez. Galván, I.; et al. OpenMolcas: From Source Code to Insight. J. Chem. Theory Comput. 2019, 15, 5925–5964. PMID: 31509407

(21) Mulliken, R. S. Intensities in Molecular Electronic Spectra X. Calculations on Mixed-Halogen, Hydrogen Halide, Alkyl Halide, and Hydroxyl Spectra. *J. Chem. Phys.* **1940**, *8*, 382–395.

(22) Escure, C.; Leininger, T.; Lepetit, B. Ab initio study of methylbromide photodissociation in the A band. *J. Chem. Phys.* **2009**, *130*, 244305.

(23) Jensen, E. T. Near-UV photodissociation of oriented CH3I adsorbed on Cu(110)-I. J. Chem. Phys. 2005, 123, 204709.

(24) Phillips, D. L.; Lawrence, B. A.; Valentini, J. J. Substituent effects on gas-phase photodissociation dynamics: resonance Raman spectra of ethyl iodide, isopropyl iodide, and tert-butyl iodide. *J. Phys. Chem.* **1991**, *95*, 9085–9091.

(25) Kavita, K.; Das, P. K. Dynamics of $I^*(2P1/2)$ production from fluorinated alkyl iodides at 266, 280, and ~ 305nm. *J. Chem. Phys.* **2000**, *112*, 8426–8431.

(26) Kim, Y. S.; Kang, W. K.; Kim, D.-C.; Jung, K.-H. Photodissociation of tert-Butyl Iodide at 277 and 304 nm: Evidence for Direct and Indirect Dissociation in A-Band Photolysis of Alkyl Iodide. J. Phys. Chem. A **1997**, 101, 7576–7581.

(27) Amatatsu, Y.; Morokuma, K.; Yabushita, S. Ab initio potential energy surfaces and trajectory studies of A-band photodissociation dynamics: CH3I* \rightarrow CH3+I and CH3+I*. *J. Chem. Phys.* **1991**, *94*, 4858–4876.

(28) Hammerich, A. D.; Manthe, U.; Kosloff, R.; Meyer, H.; Cederbaum, L. S. Time-dependent photodissociation of methyl iodide with five active modes. *J. Chem. Phys.* **1994**, *101*, 5623–5646.

(29) Mukamel, S.Principles of Nonlinear Optical Spectroscopy; Oxford University Press on Demand, 1999.

(30) Alexandre, M.; Lemercier, G.; Andraud, C.; Mesnil, H.; Schanne-Klein, M.; Hache, F. Third-order nonlinear circular dichroism in a liquid of chiral molecules. *Synth. Met.* **2002**, *127*, 135–138 Novel organic material and technological advances for photonics.

(31) Campbell, J.; Papp, T. Widths of the Atomic K-n7 Levels. Atomic Data Nucl. Data Tables 2001, 77, 1–56.

(32) Roos, B. O.; Taylor, P. R.; Sigbahn, P. E. A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approach. *Chem. Phys.* **1980**, *48*, 157–173.

(33) Malmqvist, P. A.; Rendell, A.; Roos, B. O. The restricted active space self-consistent-field method, implemented with a split graph unitary group approach. *J. Phys. Chem.* **1990**, *94*, 5477–5482.

(34) Roos, B. O.; Lindh, R.; Malmqvist, P.-k.; Veryazov, V.; Widmark, P.-O. New Relativistic ANO Basis Sets for Transition Metal Atoms. J. Phys. Chem. A 2005, 109, 6575–6579 PMID: 16834004.

(35) Almlöf, J.; Taylor, P. R. General contraction of Gaussian basis sets. I. Atomic natural orbitals for first- and second-row atoms. *J. Chem. Phys.* **1987**, *86*, 4070–4077.

(36) Dunning, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J. Chem. Phys. **1989**, 90, 1007–1023.

(37) Delcey, M. G.; Sørensen, L. K.; Vacher, M.; Couto, R. C.; Lundberg, M. Efficient calculations of a large number of highly excited states for multiconfigurational wavefunctions. *J. Comput. Chem.* **2019**, 40, 1789–1799.

(38) Wang, H.; Odelius, M.; Prendergast, D. A combined multireference pump-probe simulation method with application to XUV signatures of ultrafast methyl iodide photodissociation. *J. Chem. Phys.* **2019**, *151*, 124106.

-Supporting Information-Time-Evolving Chirality Loss in Molecular Photodissociation Monitored by X-ray Circular Dichroism Spectroscopy

Yeonsig Nam^{1,*,†}, Daeheum Cho^{2,*,†}, Bing Gu¹, Jérémy R. Rouxel³, Daniel Keefer¹, Niranjan Govind⁴, and Shaul Mukamel^{1,*}

¹Department of Chemistry, University of California, Irvine, California 92697-2025, United States ²Departments of Chemistry, Kyungpook National University, Daegu, 41566, South Korea ³University Lyon, UJM-Saint-Étienne, CNRS, Graduate School Optics Institute,

Laboratoire Hubert Curien UMR 5516, Saint-Étienne 42023, France ⁴Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, 99354, Washington, USA ⁺These authors contribute equally to this work.

Contents

Contents		S 2
1	The frequency- and time-resolved X-ray circular dichroism signal	S 3
2	Loop Diagram Rules	S 6
3	Rotational averaging	S 7
4	Supplementary Figures	S 8

1 The frequency- and time-resolved X-ray circular dichroism signal

The time-resolved X-ray circular dichroism (TRXCD) signal is given by the difference between the absorption spectra of the left and right circularly polarized probe, following excitation with an optical pump pulse. The total Hamiltonian of the system is:

$$H = H_0 + H_{\rm pu}(t) + H_{\rm pr}(t) \tag{S1}$$

where H_0 represents the Hamiltonian of a free molecule under nonadiabatic and spin-orbit couplings and

$$H_{\rm pu}(t) = -\boldsymbol{\mu} \cdot \mathbf{E}_{\rm pu}(t) - \mathbf{m} \cdot \boldsymbol{B}_{\rm pu}(t) - \boldsymbol{q} \cdot \nabla \mathbf{E}_{\rm pu}(t)$$
(S2)

$$H_{\rm pr}(t) = -\boldsymbol{\mu} \cdot \mathbf{E}_{\rm pr}(t) - \mathbf{m} \cdot \boldsymbol{B}_{\rm pr}(t) - \boldsymbol{q} \cdot \nabla \mathbf{E}_{\rm pr}(t)$$
(S3)

represents the interaction with the pump and probe, respectively. μ , **m**, and **q** are the electric dipole, magnetic dipole, and the electric quadrupole moment, respectively. We ignore the magnetic and electric quadrupole components in the pump pulse owing to their negligible contribution. **E** and **B** are the electric and magnetic fields,

$$\mathbf{E}_{s} = i \sqrt{\frac{\hbar\omega_{s}}{2\epsilon_{0}\Omega}} \hat{a}_{s} \mathbf{e}_{s} e^{i(\mathbf{k}_{s} \cdot \mathbf{r} - \omega_{s}t)} \tag{S4}$$

$$\nabla \mathbf{E}_{s} = -\sqrt{\frac{\hbar\omega_{s}}{2\epsilon_{0}\Omega}} \hat{a}_{s} (\hat{\mathbf{k}}_{s} \cdot \mathbf{e}_{s}) e^{i(\mathbf{k}_{s} \cdot \mathbf{r} - \omega_{s}t)}$$
(S5)

$$\mathbf{B}_{s} = \frac{i}{c} \sqrt{\frac{\hbar\omega_{s}}{2\epsilon_{0}\Omega}} \hat{a}_{s} (\hat{\mathbf{k}}_{s} \times \mathbf{e}_{s}) e^{i(\mathbf{k}_{s} \cdot \mathbf{r} - \omega_{s}t)}$$
(S6)

where \mathbf{k}_s is the wavevector of the emitted photon, Ω is the quantization volume, and we have the boson commutation

.

$$[a_r, a_s^{\dagger}] = \delta_{rs}. \tag{S7}$$

Note that replacing ∇E_s with $i \cdot k_s$ is valid for the slowly varying envelope approximation. Throughout this article, we assume circularly polarized probes.

$$\mathbf{E}^{L/R}(t) = a(t)\mathbf{e}_{L/R}$$
(S8)

$$\mathbf{B}^{L/R}(t) = a(t)\mathbf{b}_{L/R} \tag{S9}$$

where $\mathbf{e}_{L/R}$ and $\mathbf{b}_{L/R}$ are the polarization unit vectors of the left and right polarizations for the electric and magnetic fields, respectively. We further assumed that the Gaussian field amplitudes

$$\boldsymbol{a}_{\mathrm{pu}}(t) = a_{\mathrm{pu}} \sin(\omega_{\mathrm{pu}} t) e^{-\frac{t-t_0^2}{2\sigma_{\mathrm{pu}}^2}}$$
(S10)

$$a_{\rm pr}(t) = a_{\rm pr} e^{-\frac{(t-T)^2}{2\sigma_{\rm pr}^2}}$$
(S11)

T is the delay between the X-ray probe pulse and the optical pump that initiates chiral dynamics (see Fig. 1 (a)). The signal is measured at spectrally dispersed frequency ω and variable pump-probe time delay *T*. The time- and frequency-resolved absorption of a weak probe $A^{L/R}$ is given by[1, 2]

$$A^{L/R}(\omega, T) = 2\omega \operatorname{Im}[\mathbf{E}_{\mathrm{pr}}^{L/R*}(\omega) \cdot \mathbf{P}^{L/R}(\omega, T) + \mathbf{B}_{\mathrm{pr}}^{L/R*}(\omega) \cdot \mathbf{M}^{L/R}(\omega, T) + \nabla \mathbf{E}_{\mathrm{pr}}^{L/R*}(\omega) \cdot \mathbf{q}^{L/R}(\omega, T)]$$
(S12)

where $\mathbf{P}^{L/R}(\omega, T)$ and $\mathbf{M}^{L/R}(\omega, T)$ are the ω Fourier components of polarization and magnetization, respectively. The time- and frequency-resolved TRXCD signals are given by the difference between the absorptions of the left- and right-polarized probes.

$$S_{\text{TRXCD}} = 2\omega \text{Im}[\mathbf{E}_{\text{pr}}^{L}(\omega) \cdot \mathbf{P}^{L}(\omega, T) + \mathbf{B}_{\text{pr}}^{L}(\omega) \cdot \mathbf{M}^{L}(\omega, T) - \mathbf{E}_{\text{pr}}^{R*}(\omega) \cdot \mathbf{P}^{R}(\omega, T) - \mathbf{B}_{\text{pr}}^{R*}(\omega) \cdot \mathbf{M}^{R}(\omega, T) + \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \cdot \mathbf{q}^{L}(\omega, T) - \nabla \mathbf{E}_{\text{pr}}^{R}(\omega) \cdot \mathbf{q}^{R}(\omega, T)]$$
(S13)

Only the pseudo-scalar quantity of the signal that contains one interaction with the electric dipole (ED) and one with the magnetic dipole (MD) or the electric quadrupole (EQ) survives the rotational averaging in Eqn 13, and the signal vanishes in the dipole approximation. The interaction with the X-ray probe was calculated perturbatively using $H_{pr}(t)$. Expanding the polarization in Eqn 13 to the first order in the probe field leads to

$$\begin{split} S_{\text{TRXCD}} &= 2\omega \text{Re} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int_{0}^{t} dt_{1} \\ & \langle \Psi_{0} | U^{\dagger}(t,0) \mu^{\dagger} U(t,t_{1}) \mathbf{m} U(t_{1},0) | \Psi_{0} \rangle_{\Omega} \mathbf{E}_{\text{pr}}^{L*}(\omega) \otimes \mathbf{B}_{\text{pr}}^{L}(t_{1},T) \\ & + \langle \Psi_{0} | U^{\dagger}(t,0) \mathbf{m}^{\dagger} U(t,t_{1}) \mu U(t_{1},0) | \Psi_{0} \rangle_{\Omega} \mathbf{B}_{\text{pr}}^{L*}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{m}^{\dagger} U^{\dagger}(t,t_{1}) \mu U(t,0) | \Psi_{0} \rangle_{\Omega} \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{B}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t,0) \mu^{\dagger} U^{\dagger}(t,t_{1}) \mathbf{m} U(t,0) \mu | \Psi_{0} \rangle_{\Omega} \mathbf{E}_{\text{pr}}^{L*}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & + \langle \Psi_{0} | U^{\dagger}(t,0) \mu^{\dagger} U(t,t_{1}) \mathbf{q} U(t_{1},0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L*}(\omega) \otimes \nabla \mathbf{E}_{\text{pr}}^{L}(t_{1},T) \\ & + \langle \Psi_{0} | U^{\dagger}(t,0) \mathbf{q}^{\dagger} U(t,t_{1}) \mu U(t_{1},0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L*}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mu U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L*}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mu U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mathbf{q} U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mathbf{q} U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mathbf{q} U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mathbf{q} U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{q}^{\dagger} U^{\dagger}(t,t_{1}) \mathbf{q} U(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t_{1},0) \mathbf{e}_{0} \langle U^{\dagger}(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{\text{pr}}^{L}(\omega) \otimes \mathbf{E}_{\text{pr}}^{L*}(t_{1},T) \\ & - \langle \Psi_{0} | U^{\dagger}(t,0) - \mathbf{E}_{0} \langle U^{\dagger}(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{0} \langle U^{\dagger}(t,0) | \Psi_{0} \rangle_{\Omega} \nabla \mathbf{E}_{0} \langle U^{\dagger}(t,0) \rangle_{\Omega} \\ & = 4\omega \text{Im} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int_{0}^{t} dt_{1}$$

The first four terms correspond to the top four loop diagrams in Figure S1 and the last four terms correspond to the bottom four loop diagrams. $U(t, t_1)$ is the time evolution operator between times t and t_1 and $|\Psi_0\rangle$ is the matter ground-state wavefunction. L \leftrightarrow R represents the terms in Eqn S14 with right polarization instead of left. $\langle \cdot \cdot \cdot \rangle_{\Omega}$ represents rotational averaging over the material quantities. The interaction with the pump is treated non-perturbatively and included directly in the propagator U of the system. We define the electric dipole-magnetic dipole (ED-MD), magnetic

dipole-electric dipole (MD-ED), electric dipole-electric dipole (ED-ED), and electric dipole-electric quadrupole (ED-QD) response functions by

$$\mathbf{R}_{em}(t,t_1) = \langle \Psi_0 | U^{\dagger}(t,0) \boldsymbol{\mu}^{\dagger} U(t,t_1) \mathbf{m} U(t_1,0) | \Psi_0 \rangle_{\Omega}$$
(S16)

$$\mathbf{R}_{me}(t,t_1) = \langle \Psi_0 | U^{\dagger}(t,0) \mathbf{m}^{\dagger} U(t,t_1) \boldsymbol{\mu} U(t_1,0) | \Psi_0 \rangle_{\Omega}$$
(S17)
$$\mathbf{R}_{me}(t,t_1) = \langle \Psi_0 | U^{\dagger}(t,0) \mathbf{m}^{\dagger} U(t,t_1) \boldsymbol{\mu} U(t_1,0) | \Psi_0 \rangle_{\Omega}$$
(S17)

$$\mathbf{R}_{ee}(t,t_1) = \langle \Psi_0 | U^{\dagger}(t,0) \boldsymbol{\mu}^{\dagger} U(t,t_1) \boldsymbol{\mu} U(t_1,0) | \Psi_0 \rangle_{\Omega}$$
(S18)

$$\mathbf{R}_{eq}(t,t_1) = \langle \Psi_0 | U^{\dagger}(t,0) \boldsymbol{\mu}^{\dagger} U(t,t_1) \mathbf{q} U(t_1,0) | \Psi_0 \rangle_{\Omega}$$
(S19)

$$\mathbf{R}_{qe}(t,t_1) = \langle \Psi_0 | U^{\mathsf{T}}(t,0) \mathbf{q}^{\mathsf{T}} U(t,t_1) \mu U(t_1,0) | \Psi_0 \rangle_{\Omega}$$
(S20)

where $|\Psi(\mathbf{r}, \mathbf{R}, t)\rangle$ represents the free evolution of the system following the pump pulse. This is expanded based on $|\varphi_i(\mathbf{r}, \mathbf{R})\rangle$ of the adiabatic electronic state (abbreviated as $|i\rangle$ below)

$$|\Psi(\mathbf{r},\mathbf{R},t)\rangle = \sum_{i} c_{i}(t)|\chi_{i}(\mathbf{R},t)\rangle|\varphi_{i}(\mathbf{r},\mathbf{R})\rangle$$
(S21)

where $\chi_i(\mathbf{R}, t)$ is the time-dependent normalized nuclear wavepacket on the valence potential energy surface *i* with the amplitude of the adiabatic surface $c_i(t)$. Then, equations S17–S20 can be expanded as

$$\mathbf{R}_{em}(t,t_1) = \sum_{ij} \langle \Psi_0(t) | j \rangle \boldsymbol{\mu}_{jc}^{\dagger}(t) \langle c | \boldsymbol{U}(t,t_1) | c \rangle \mathbf{m}_{ci}(t_1) \langle i | \Psi_0(t_1) \rangle$$
$$= \sum_{ij} c_i(t_1) c_j^*(t) \langle \chi_j(t) | \chi_i(t_1) \rangle \boldsymbol{\mu}_{jc}^{\dagger}(t) \mathbf{m}_{ci}(t_1) e^{-i\omega_c(t-t_1)}$$
(S22)

$$\mathbf{R}_{me}(t,t_1) = \sum_{ij} \langle \Psi_0(t) | j \rangle \mathbf{m}_{jc}^{\dagger}(t) \langle c | U(t,t_1) | c \rangle \boldsymbol{\mu}_{ci}(t_1) \langle i | \Psi_0(t_1) \rangle$$

$$= \sum_{ij} c_i(t_1) c_j^*(t) \langle \chi_j(t) | \chi_i(t_1) \rangle \mathbf{m}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1) e^{-i\omega_c(t-t_1)}$$
(S23)

$$\mathbf{R}_{ee}(t,t_1) = \sum_{ij} \langle \Psi_0(t) | j \rangle \boldsymbol{\mu}_{jc}^{\dagger}(t) \langle c | U(t,t_1) | c \rangle \boldsymbol{\mu}_{ci}(t_1) \langle i | \Psi_0(t_1) \rangle$$
$$= \sum_{ij} c_i(t_1) c_j^{*}(t) \langle \chi_j(t) | \chi_i(t_1) \rangle \boldsymbol{\mu}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1) e^{-i\omega_c(t-t_1)}$$
(S24)

$$\mathbf{R}_{eq}(t,t_1) = \sum_{ij} \langle \Psi_0(t) | j \rangle \boldsymbol{\mu}_{jc}^{\dagger}(t) \langle c | U(t,t_1) | c \rangle \mathbf{q}_{ci}(t_1) \langle i | \Psi_0(t_1) \rangle$$
$$= \sum_{ij} c_i(t_1) c_j^{*}(t) \langle \chi_j(t) | \chi_i(t_1) \rangle \boldsymbol{\mu}_{jc}^{\dagger}(t) \mathbf{q}_{ci}(t_1) e^{-i\omega_c(t-t_1)}$$
(S25)

$$\mathbf{R}_{qe}(t,t_1) = \sum_{ij} \langle \Psi_0(t) | j \rangle \mathbf{q}_{jc}^{\dagger}(t) \langle c | U(t,t_1) | c \rangle \boldsymbol{\mu}_{ci}(t_1) \langle i | \Psi_0(t_1) \rangle$$
$$= \sum_{ij} c_i(t_1) c_j^{*}(t) \langle \chi_j(t) | \chi_i(t_1) \rangle \mathbf{q}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1) e^{-i\omega_c(t-t_1)}$$
(S26)

Using eqs. S22-S26, eq. S15 can be rewritten as

$$S_{\text{TRXCD}} = 4\omega \text{Im} \int_{-\infty}^{\infty} dt e^{-i(\omega-\omega_c)t} \int_{0}^{t} dt_1$$

$$\sum_{ij} c_i(t_1) c_j^*(t) \langle \chi_j(t) | \chi_i(t_1) \rangle [\boldsymbol{\mu}_{jc}^{\dagger}(t) \mathbf{m}_{ci}(t_1) - \mathbf{m}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1)$$

$$+ i\omega (\boldsymbol{\mu}_{jc}^{\dagger}(t) \mathbf{q}_{ci}(t_1) - \mathbf{q}_{jc}^{\dagger}(t) \boldsymbol{\mu}_{ci}(t_1))] a(\omega) a(t_1 - T) e^{-i(\omega_c - \omega_{\text{pr}})t_1}$$
(S27)

In the impulsive limit $a(t_1 - T) = \delta(T)a$, where $t_1 \to 0$. We further describe the quantities t_1 as electronic modulations, for example, $c_i(t_1) = c_i(t)e^{i\omega_i t_1}$. We introduce the lifetime broadenings 0.100 eV (for C 1s edge) and 1.53 eV (I 2s edge) for Γ_c [3]. The Fourier transform of the probe pulse in the time domain to the frequency domain yields

$$\int_0^\infty e^{i(\omega_{\rm pr}-\omega_{ci}+i\Gamma_{ci})t_1} = \frac{-i}{\omega_s - \omega_{ci} + i\Gamma_{ci}}$$
(S28)

Finally, the signal reads as follows:

$$S_{\text{TRXCD}}(\omega_s, T) = -4\omega \operatorname{Re}a(\omega_s) a^*(\omega_s) \sum_{ijc} c_i(T) c_j^*(T) \langle \chi_j(T) | \chi_i(T) \rangle$$
(S29)

$$\times \left[\frac{\boldsymbol{\mu}_{jc}^{\dagger}(T)\boldsymbol{m}_{ci}(T) - \boldsymbol{m}_{jc}^{\dagger}(T)\boldsymbol{\mu}_{ci}(T) + i\omega_{s}[\boldsymbol{\mu}_{jc}^{\dagger}(T)\boldsymbol{q}_{ci}(T) - \boldsymbol{q}_{jc}^{\dagger}(T)\boldsymbol{\mu}_{ci}(T)]}{\omega_{s} - \omega_{ci} + i\Gamma_{ci}}\right]$$
(S30)

As a reference, we present the non-chiral pump-probe signal (transient X-ray absorption, TRXAS), which is calculated by considering only the electric-electric contribution:

$$S_{\text{TRXAS}}(\omega_s, T) = -4\omega \text{Im}a(\omega_s)a^*(\omega_s) \sum_{ijc} \frac{c_i(T)c_j^*(T)\langle\chi_j(T)|\chi_i(T)\rangle \times \mu_{jc}^{\dagger}(T)\mu_{ci}(T)}{\omega_s - \omega_{ci} + i\Gamma_{ci}}$$
(S31)

2 Loop Diagram Rules

The loop diagram of the optical pump-resonant X-ray probe signal is shown in Figure S1. The Diagram rules are as follows:

- Time runs along the loop clockwise from bottom left to bottom right.
- Each field interaction is represented by an arrow, which either points to the right (photon annihilation and excitation of the molecule) or to the left (photon creation and de-excitation of the molecule).
- Free evolution periods on the left branch indicate forward propagation in real time, and on the right branch to backward propagation, respectively.
- The last field interaction is the detected photon mode. In addition, the gray bar represents the period of free evolution.

3 Rotational averaging

A *n*-th rank tensor *T* is rotationally averaged using the averaging tensor $I^{(n)}$. The correlation tensor involving electric and magnetic dipoles are only fourth rank tensors for TRXCD and the ones involving electric quadrupole are of rank 5.

$$I^{(4)} = \frac{1}{30} \begin{pmatrix} \delta_{ij} \delta_{kl} \\ \delta_{ik} \delta_{jl} \\ \delta_{il} \delta_{jk} \end{pmatrix}^{T} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{i'j'} \delta_{k'l'} \\ \delta_{i'k'} \delta_{j'l'} \\ \delta_{i'l'} \delta_{j'k'} \end{pmatrix}$$
(S32)

$$I^{(5)} = \frac{1}{30} \begin{pmatrix} \varepsilon_{ijk} \delta_{nm} \\ \varepsilon_{ijn} \delta_{km} \\ \varepsilon_{ijm} \delta_{kn} \\ \varepsilon_{ikm} \delta_{jm} \\ \varepsilon_{ikm} \delta_{jn} \\ \varepsilon_{inm} \delta_{jk} \end{pmatrix}^{T} \begin{pmatrix} 3 & -1 & -1 & 1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{pmatrix} \begin{pmatrix} \varepsilon_{i'j'k'} \delta_{n'm'} \\ \varepsilon_{i'j'm'} \delta_{k'n'} \\ \varepsilon_{i'k'm'} \delta_{j'm'} \\ \varepsilon_{i'k'm'} \delta_{j'm'} \\ \varepsilon_{i'n'm'} \delta_{j'n'} \\ \varepsilon_{i'n'm'} \delta_{j'k'} \end{pmatrix}$$
(S33)

where δ and ε are the Kronecker and Levi-Civita symbols respectively, and *T* means transpose. The $I^{(4)}$ tensor is used to rotationally average the magnetic correlation functions (e.g. $\langle \mu\mu\mu m \rangle$) and $I^{(5)}$ for the electric quadrupole ones (e.g. $\langle \mu\mu\mu q \rangle$). For example, we have

$$(\langle \mu\mu\mu\mu\rangle_{\Omega})_{ijkl} = (I^{(4)})^{i'j'k'l'}_{ijkl} \langle \mu\mu\mu\rangle_{i'j'k'l'}$$
(S34)

$$(\langle \mu\mu\mu q \rangle_{\Omega})_{ijknm} = (I^{(5)})^{i'j'k'n'm'}_{ijknm} \langle \mu\mu\mu q \rangle_{i'j'k'n'm'}$$
(S35)

where we used Einstein summation convention for the Cartesian indices *i*, *j*, *k*, *l*, *n*, and *m* and $\langle ... \rangle_{\Omega}$ stands for rotational averaging.

4 Supplementary Figures



Figure S 1: Loop diagrams contributing to the time-resolved circular dichroism signal. Diagrams (i)-(iv) represent the electric dipole - magnetic dipole contributions and diagrams (v)-(viii) the electric dipole- electric quadrupole ones. Diagrams (i), (ii), (v), and (vi) represent stimulated Raman, (iii), (iv), (vii), and (viii) represent the excited state absorption. Arrows represent the interactions with the probe. The shaded area represents the initial preparation process by the pump and the free evolution of the molecule.

References

- [1] Shaul Mukamel. *Principles of nonlinear optical spectroscopy*. 6. Oxford University Press on Demand, 1999.
- [2] M. Alexandre et al. "Third-order nonlinear circular dichroism in a liquid of chiral molecules". In: Synthetic Metals 127.1 (2002). Novel organic material and technological advances for photonics, pp. 135–138. ISSN: 0379-6779. DOI: https://doi.org/10.1016/S0379-6779(01) 00604-X. URL: https://www.sciencedirect.com/science/article/pii/S037967790100604X.



Figure S 2: The expectation value of C-I distance for the wavepackets evolving on the (a) total, (b) ground state, and (c) excited states. The ground state nuclear WP oscillates within the potential well while the excited state nuclear WPs propagate to the elongated C-I reactive coordinates.

[3] J.L. CAMPBELL and TIBOR PAPP. "WIDTHS OF THE ATOMIC K-N7 LEVELS". In: Atomic Data and Nuclear Data Tables 77.1 (2001), pp. 1-56. ISSN: 0092-640X. DOI: https://doi.org/ 10.1006/adnd.2000.0848. URL: https://www.sciencedirect.com/science/article/pii/ S0092640X00908489.



Figure S 3: (a) Frequency- and time-resolved X-ray absorption signal at iodine L_1 edge, dissected into contribution of $\mu^+ m - m^+ \mu$ response in population (b) and in coherence (c), and $\mu^+ q - q^+ \mu$ response in (d) population and (e) coherence. Strong $\mu^+ q - q^+ \mu$ response from coherence (e) dominates the total signal



Figure S 4: The TRXCD signal above iodine 2s edge dissected into contribution of each core states; (a) SC₁, (b) TC₁, (c) SC₂, and (d) SC₃ core excited state. In the middle and bottom panels, the valence coherences which contribute most to the TRXCD signal are displayed. The TRXCD signal involving SC₁/TC₁ is observed at 5226 eV, while that involving SC_{2/3} at 5232 eV.



Figure S 5: Same for Figure S3 but for C₁ 1s edge. Strong $\mu^{\dagger}m - m^{\dagger}\mu$ response from population (b) dominates the total signal



Figure S 6: The TRXCD signal above C_1 1s edge. (a) Figure 5b between T = 80 to 160 fs was enlarged and rescaled to visualize the absorptive signature from the 3Q_0 population at 259.5 eV. (b) coherence contribution to the signal. The intensity is around two orders of magnitude smaller than population contribution. The spectroscopic signature from ${}^3Q_0/{}^3Q_1$ coherence is observed at 259.5 eV with oscillating pattern, while that from ${}^1Q_1/{}^3Q_1$ is observed at 260.3 eV with constant negative feature.