Revealing electronic state-switching at conical intersections in alkyl iodides by ultrafast XUV transient absorption spectroscopy

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Conical intersections between electronic states often dictate the chemistry of photoexcited molecules. Recently developed sources of ultrashort extreme ultraviolet (XUV) pulses tuned to element-specific transitions in molecules allow for the unambiguous detection of electronic state-switching at a conical intersection. Here, the fragmentation of photoexcited iso-propyl iodide and tert-butyl iodide molecules (i-C3H7I and t-C4H9I) through a conical intersection between 3Q0/1Q1 spin-orbit states is revealed by ultrafast XUV transient absorption measuring iodine 4d core-to-valence transitions. The electronic state-sensitivity of the technique allows for a complete mapping of molecular dissociation from photoexcitation to photoproducts. In both molecules, the sub-100 fs transfer of a photoexcited wave packet from the 3Q0 state into the 1Q1 state at the conical intersection is captured. The results show how differences in the electronic state-switching of the wave packet in i-C3H7I and t-C4H9I directly lead to differences in the photoproduct branching ratio of the two systems.
The coupled evolution of electronic and nuclear structures plays a fundamental role in molecular reactions. The dynamics of chemical reactions are traditionally viewed within the Born–Oppenheimer approximation, which assumes separation of nuclear and electronic degrees of freedom in the system. While often applicable to reactions in ground electronic states, this approximation is frequently insufficient to describe excited state dynamics following photoexcitation where extensive couplings between electron and nuclear motions arise\(^1\). At crossings between the potential energy surfaces of electronic states where conical intersections are formed, the presence of strong couplings allow a molecule to abruptly transfer from one surface to another, thereby switching its electronic character. Due to the ubiquitous occurrence of crossings among electronically-excited states, the chemical outcomes of many photoinduced processes such as DNA photoprotection\(^5,6\) and retinal isomerization in vision\(^7,8-9\) are dictated by nonadiabatic state-switching at conical intersections.

Nonadiabatic dynamics at conical intersections are often challenging to capture experimentally as they necessarily involve multiple electronic states and typically evolve on a sub-ps timescale. Extreme ultraviolet (XUV) and soft X-ray absorption spectroscopies that measure resonant transitions from atomic core orbitals into unoccupied valence orbitals provide sensitivity to the symmetries, orbital occupations, and spin characteristics of electronic states\(^10-16\). Emerging femtosecond and attosecond transient absorption spectroscopies based on core-to-valence transitions therefore offer a powerful means of resolving multistate dynamics with excellent temporal resolution, enabling observations of rapid electronic state-switching at conical intersections which have previously eluded experimental observation.

The alkyl iodides (R-I, R \(\approx C_nH_m\)) constitute an important class of molecules for the investigation of nonadiabatic dynamics, as their dissociation in the A-band is intrinsically controlled by a conical intersection\(^17-24\). The A-band comprises dissociative spin–orbit states accessed by \(5p \rightarrow \sigma^*\) valence excitation in the ultraviolet (UV) from a nonbonding iodine orbital into an antibonding orbital along the C–I bond. UV excitation results in rapid cleavage of the C–I bond within \(200 \text{ fs}\)\(^25\). Within the excitation, spin–orbit states carrying the Mulliken labels \(3Q_0, 1Q_1,\) and \(3Q_1\) are optically accessible\(^26\) (Supplementary Note 1). For few-carbon containing alkyl iodides, excitation to \(3Q_0\) comprises 70–80% of the oscillator strength in the A-band\(^21,26,27\). As shown schematically in Fig. 1a, UV excitation prepares an electronic–nuclear wave packet on the \(3Q_0\) surface correlating to the production of spin–orbit excited \(1^e(2P_{3/2})\) atoms. Throughout its motion along the steeply repulsive potential, a fraction of the initially prepared wave packet can cross to the \(1Q_1\) surface via a conical intersection, allowing for the release of ground state \(1^e(2P_{3/2})\) atoms. Consequently, the production of atomic I photo-products has been primarily attributed to nonadiabatic \(3Q_0/1Q_1\) state-switching via the conical intersection\(^19,21,28-30\).

The \(1^e\) photoproduct branching ratio varies widely among alkyl iodides depending on R-group structure. Previously-measured \(1^e\) branching ratios obtained from the dissociation of several alkyl iodides at 277–280 nm are plotted in Fig. 1b. Methyl and ethyl iodide (CH\(_3\)I and C\(_2\)H\(_5\)I) dissociation forms atomic I in a minority ratio of \(~1:3\) relative to \(1^e\) \(\approx 31,32\). In contrast, the dissociation of molecules with greater methyl substitution at the central carbon favors the release of atomic I. For i-C\(_3\)H\(_7\)I, atomic I photoproducts dominate in a ratio of \(~2:1\)\(^{33}\), while t-C\(_4\)H\(_9\)I provides an even greater yield of \(~13:1\)\(^{29,34}\). The dramatic increase in atomic I production suggests that a significantly larger fraction of the initial wave packet switches to the \(1Q_1\) state while passing through the conical intersection\(^19,29,34\). While i-C\(_3\)H\(_7\)I appears to represent an intermediate case in which the wave packet bifurcates between the \(1Q_1\) and \(3Q_0\) states in a \(~2:1\) ratio, t-C\(_4\)H\(_9\)I appears to represent a case of nearly-complete transfer to the \(1Q_1\) state.

Due to the ubiquitous occurrence of crossings among electronically-excited states, the chemical outcomes of many photoinduced processes such as DNA photoprotection\(^5,6\) and retinal isomerization in vision\(^7,8-9\) are dictated by nonadiabatic state-switching at conical intersections.

In this report, ultrafast XUV transient absorption spectroscopy is applied to the investigation of the \(3Q_0/1Q_1\) conical intersection dynamics in i-C\(_3\)H\(_7\)I and t-C\(_4\)H\(_9\)I. Experimentally, dynamics are launched by a resonant femtosecond UV pump pulse and followed by a time-delayed attosecond XUV pulse that probes transitions between iodine I(4\(d\)) core orbitals and valence orbitals of the dissociating molecules (Fig. 1a). In the corresponding XUV absorption spectra, regions of the excited state surfaces both prior and subsequent to the conical intersection are mapped to distinct spectral features, which allows for the unambiguous detection of electronic state-switching at the conical intersection correlating with the release of atomic I\(^{*}\) and I. The signatures of conical intersection dynamics and molecular fragmentation are found to be in excellent agreement with simulated XUV spectra of a CH\(_3\)I model system.

**Results**

**Time-resolved probing of iso-propyl and tert-butyl iodide**

The experimental pump-probe setup is summarized in Fig. 1c–e. Additional details of the experimental apparatus can be found in the “Methods” section. Briefly, gaseous i-C\(_3\)H\(_7\)I and t-C\(_4\)H\(_9\)I molecules in a quasi-static gas cell are excited by UV pump pulses (277 nm, 50 fs, 5 \(\mu\)J per pulse) at a peak intensity of \(1.1 \times \times 10^{12} \text{ W cm}^{-2}\). The UV pump spectrum is centered near the 260 and 268 nm A-band absorption maxima of \(i\)-C\(_3\)H\(_7\)I and t-C\(_4\)H\(_9\)I, respectively\(^40\). Following UV excitation, dynamics are probed by time-delayed isolated attosecond XUV pulses (40–70 eV, \(~170 \text{ as}\)\(^{31}\)) tuned to absorption transitions from the \(1A_d\) core orbital appearing in the 45–48 eV photon energy range. A Gaussian instrument response function of \(50 \pm 7 \text{ fs}\) (full width at half maximum) of the transient absorption experiment is measured using an in situ UV-XUV cross-correlation method.

As shown in Fig. 1a, wave packet motion from the highly repulsive region of the excited state surfaces (Regions 1–2) into the asymptotic dissociation limit (Region 3) is probed through XUV absorption transitions corresponding to core-to-valence excitations primarily localized on iodine. The \(3Q_0\) and \(1Q_1\) excited states are characterized by the configuration \((4d_{4/2}^0)(\sigma^*)^0(3p^{2}\sigma^*)\) where the nonbonding \(5p\) valence orbitals on iodine possess \(5p\sigma^*\) character due to interactions with the alkyl moiety. In a one-electron transition picture\(^35,38,39\), the excited states can be probed by the excitation of available \(4d \rightarrow 5p\) transitions to distinct \((4d_{4/2})^{-1}\sigma^*\) and \((4d_{4/2})^{-1}\sigma^*\) core-excited states separated in energy by the \(4d\) core-hole spin–orbit splitting. In the corresponding XUV absorption spectra, transitions appear as doublets with excitations to \((4d_{4/2})^{-1}\sigma^*\) appearing at higher photon energies compared to excitations to \((4d_{5/2})^{-1}\sigma^*\). In Fig. 1a, stronger and weaker XUV transitions are distinguished by solid and dashed arrows. In this study, the \(3Q_0\) state primarily undergoes strong transitions to the \((4d_{5/2})^{-1}\sigma^*\) state appearing at higher XUV energies in the spectrum, whereas the \(1Q_1\) state primarily undergoes strong transitions to the \((4d_{4/2})^{-1}\sigma^*\) state.
appearing at lower XUV energies due to spin–orbit selection rules imparted by the iodine atom. In addition to their primary appearance at distinct photon energies, dynamics along the $3Q_0$ and $1Q_1$ potentials are further distinguished by their evolution at long-time delays. During molecular fragmentation along the C–I bond, the collapse of the hybridized molecular orbitals surrounding the iodine atom leading to a purely-atomic (4d)$^-$ configuration is spectroscopically revealed through the convergence of molecular $3Q_0$ and $1Q_1$ features into peaks associated with free I* and I atoms at long-time delays.

Transient absorption spectra are recorded as changes in optical density $\Delta OD = \log([I_{XUV,UV}(E, \tau)]/I_{XUV}(E))$, where $I_{XUV,UV}(E, \tau)$ is the XUV spectrum recorded at the time delay $\tau$ following the UV pump and $I_{XUV}(E)$ is the XUV spectrum recorded in the absence of the pump. The scan averages and integration times used to record the experimental transients are described in the "Methods" section. To eliminate high-frequency noise, the recorded transients are post processed using a low pass filter (Supplementary Note 2). After post processing, the experimental noise level is estimated as $\approx$2 mOD. In Fig. 3a–d, the resulting transients for $i$-$C_3H_7$I and $i$-$C_4H_9$I are plotted between 44.5 and 48.5 eV photon energies where time-dependent features that reflect excited state dynamics are observed. Spectra plotted over the full photon energy range recorded (44–60 eV) can be found in Supplementary Figs. 1, 2.

Experimental spectra plotted at time delay intervals between $–4$ and 160 fs are shown in Fig. 2a, b. Several discrete, time-dependent features are observed in the spectra. The rich evolution of the features can be observed in the colormap depictions of the transient spectra shown in Fig. 2c, d. The convergence of features at early time delays (0–100 fs) into the fixed values of atomic transitions at longer times (100–160 fs) reflects dynamics evolving from the steeply repulsive to the asymptotic regions of the excited state potentials. In particular, dissociation in the asymptotic region (Region 3, Fig. 1a) is significantly delayed in the $i$-$C_4H_9$I transient, atomic I and I* peaks are observed. The intensities of the observed atomic transitions allow branching ratio estimates of $\approx$2:1 for $i$-$C_3H_7$I and $i$-$C_4H_9$I as consistent with the I:I* branching ratio data (277–280 nm excitation) obtained from refs. 29,31–33 and plotted as a function of methyl substitutions. The molecular structures of the alkyl iodides are depicted with carbon atoms in gray, hydrogen atoms in white, and iodine atoms in magenta.

**Fig. 1 A-band fragmentation of alkyl iodides and experimental outline. a** Potential energy curves adapted from ref. 25 are plotted as a function of C–I distance. The $3Q_0$/1Q_1 conical intersection (dotted circle) allows for wave packet bifurcation into I* and I dissociation channels. The partitioning of available energy into different degrees of freedom is not represented in this schematic. Dynamics along the $3Q_0$ and $1Q_1$ potentials before the conical intersection (Region 1), after the conical intersection (Region 2), and in the dissociation limit (Region 3) are mapped through XUV transitions to core-excited molecular states labeled (4i$^-$)$^1$–$\sigma^*(\approx)$ character. The molecular core-excited states connect to atomic (4i$^-$)$^1$–$\sigma^*$ character.

The XUV probe spectrum is recorded at the time delay $\tau$ following the UV pump. The scan averages and integration times used to record the experimental transients are described in the "Methods" section. To eliminate high-frequency noise, the recorded transients for $i$-$C_3H_7$I and $i$-$C_4H_9$I are plotted between 44.5 and 48.5 eV photon energies due to spin–orbit selection rules imparted by the iodine atom. In addition to their primary appearance at distinct photon energies, dynamics along the $3Q_0$ and $1Q_1$ potentials are further distinguished by their evolution at long-time delays. During molecular fragmentation along the C–I bond, the collapse of the hybridized molecular orbitals surrounding the iodine atom leading to a purely-atomic (4d)$^-$ configuration is spectroscopically revealed through the convergence of molecular $3Q_0$ and $1Q_1$ features into peaks associated with free I* and I atoms at long-time delays.

Transient absorption spectra are recorded as changes in optical density $\Delta OD = \log([I_{XUV,UV}(E, \tau)]/I_{XUV}(E))$, where $I_{XUV,UV}(E, \tau)$ is the XUV spectrum recorded at the time delay $\tau$ following the UV pump and $I_{XUV}(E)$ is the XUV spectrum recorded in the absence of the pump. The scan averages and integration times used to record the experimental transients are described in the "Methods" section. To eliminate high-frequency noise, the recorded transients are post processed using a low pass filter (Supplementary Note 2). After post processing, the experimental noise level is estimated as $\approx$2 mOD. In Fig. 3a–d, the resulting transients for $i$-$C_3H_7$I and $i$-$C_4H_9$I are plotted between 44.5 and 48.5 eV photon energies where time-dependent features that reflect excited state dynamics are observed. Spectra plotted over the full photon energy range recorded (44–60 eV) can be found in Supplementary Figs. 1, 2.

Experimental spectra plotted at time delay intervals between $–4$ and 160 fs are shown in Fig. 2a, b. Several discrete, time-dependent features are observed in the spectra. The rich evolution of the features can be observed in the colormap depictions of the transient spectra shown in Fig. 2c, d. The convergence of features at early time delays (0–100 fs) into the fixed values of atomic transitions at longer times (100–160 fs) reflects dynamics evolving from the steeply repulsive to the asymptotic regions of the excited state potentials. In particular, dissociation in the asymptotic region (Region 3, Fig. 1a) is significantly delayed in the $i$-$C_4H_9$I transient, atomic I and I* peaks are observed. The intensities of the observed atomic transitions allow branching ratio estimates of $\approx$2:1 for $i$-$C_3H_7$I and $i$-$C_4H_9$I as consistent with the I:I* branching ratio data (277–280 nm excitation) obtained from refs. 29,31–33 and plotted as a function of methyl substitutions. The molecular structures of the alkyl iodides are depicted with carbon atoms in gray, hydrogen atoms in white, and iodine atoms in magenta.
(Fig. 2a–d), discrete molecular features located at 47.1 and 45.4 eV are transiently observed. While the two features both rise and decay within 100 fs, they otherwise exhibit different dynamics. The 47.1 eV feature is observed to maximize in intensity within the instrument response function. In contrast, the 45.4 eV feature maximizes in intensity 25 fs later, and its rise thus accompanies the decay of the 47.1 eV feature. Furthermore, the two features converge to different atomic absorption lines in the long-time limit. In the i-C₃H₇I transient where both 1ᵢ and Iᵢ peaks are observed, the 47.1 and 45.4 eV features exhibit clear shifts in energy into the Iᵢ (46.7 eV) and I(45.9 eV) lines, respectively (Supplementary Fig. 3). In the i-C₄H₉I transient where only Iᵢ peaks are observed, the 45.4 eV feature shifts into the I(45.9 eV) absorption line whereas the 47.1 eV feature disappears with no accompanying Iᵢ rise. The molecular features at 47.1 and 45.4 eV are therefore assigned to 3Q₀ and 1Q₁ states, respectively. In accordance with its prompt appearance, the 47.1 eV (3Q₀) feature is assigned to the region before the conical intersection (Region 1) directly populated by the UV pump. Meanwhile, the 45.4 eV (1Q₁) feature is ascribed to the region after the conical intersection (Region 2) populated through nonadiabatic transitions from the 3Q₀ state at later times. Based on an analysis of time traces taken at 47.1 eV in the molecular transients (Supplementary Fig. 4), 3Q₀ population is found to decay through state-switching at the conical intersection with a τCI = 36 ± 4 fs exponential time constant in i-C₃H₇I and τCI ≤ 67 ± 6 fs exponential time constant in i-C₄H₉I (Supplementary Table 1). Although exponential time constants associated with state-switching at the conical intersection can also be obtained from time traces at 45.4 eV in the molecular transients, the analysis is currently limited by the temporal resolution of the experiments.

The concomitant decay and rise of the state-specific molecular signals in the XUV, appearing as a discontinuous switching of intensity from the 3Q₀ (Region 1) feature to the 1Q₁ (Region 2) feature in the transients, provides a clear spectroscopic signature of electronic reconfiguration at a conical intersection. Following passage through the conical intersection, dissociation dynamics along the 3Q₀ and 1Q₁ potentials (Regions 2–3) are mapped through continuous shifts into corresponding atomic Iᵢ and I absorption lines in the long-time limit. Thus, the ability of XUV spectroscopy to temporally and energetically resolve all electronic states involved in the reaction allows for the complete mapping of molecular fragmentation dynamics in the A-band, including the critical moment of wave packet bifurcation at the conical intersection.
intersection. The experimental XUV transients obtained exemplify the cases of intermediate and nearly-complete electronic reconfiguration at a conical intersection. In the case of i-C₃H₇I–I (Fig. 2c), intermediate state-switching resulting in the partial retention of population on Q₀ after the conical intersection is directly observed as the spectral feature connecting the Q₀ (Region 1) signal to the atomic I² limit. In contrast, the nearly-complete transfer of population from Q₂ to Q₁ in t-C₄H₉I (Fig. 2d) is signified by the abrupt disappearance of the Q₀ (Region 1) signal.

As shown in the experimental schematic in Fig. 1a, dynamics are followed through excitations to (4d₃/₂)−1σ⁺ and (4d₅/₂)−1σ⁺ core-excited states. The 47.1 eV (Q₀) signal can be assigned to (4d₃/₂)−1σ⁺ excitation based on its I²(2P₃/₂)−→2D₅/₂ convergence limit. Similarly, the 45.4 eV (Q₁) feature can be assigned to (4d₅/₂)−1σ⁺ excitation based on its I²(2P₃/₂)−→2D₅/₂ convergence limit. In principle, complementary Q₂ and Q₁ transitions associated with (4d₃/₂)−1σ⁺ and (4d₅/₂)−1σ⁺ excitations, respectively, are also possible. Such transitions would appear as continuous signals connecting the 45.4 eV (Q₁) feature at early times to the atomically-forbidden 45.0 eV [I²(2P₃/₂)−→2D₅/₂] convergence limit, and connecting the 47.1 eV (Q₀) feature to the weakly-allowed 47.6 eV [I²(2P₃/₂)−→2D₅/₂] convergence limit. However, no such signals are observed in the experimental results (Fig. 2a–d) and are presumed to be too weak to be detected. Instead, the selective detection of structural dynamics within the R-group moiety of the alkyl iodides during C–I dissociation, thus providing a multi-dimensional picture of passage through the conical intersection. Finally, the application of ultrafast XUV transient absorption methodologies to classes of molecules beyond alkyl iodides will continue to provide a powerful route for the direct investigation of non-Born–Oppenheimer dynamics governing the chemistry of electronically-excited systems.

Methods

Experimental setup. The i-C₃H₇I and t-C₄H₉I molecules are obtained from Sigma-Aldrich at 99% and 95% purity, respectively. The sample target consists of a 3 mm long quasi-static gas cell filled with 1 atm of alkyl iodide molecules, allowing for the UV pump and XUV probe pulses to be simultaneously isolated attosecond XUV pulses are generated through amplitude gating. The UV pump and XUV probe pulses are generated through amplitude gating. The spectrum of the attosecond XUV pulses exhibits a smooth continuum structure between 40 and 70 eV. According to previous streaking measurements, the XUV pulse duration is estimated to be ~170 as. Residual NIR light is subsequently removed from the XUV beam path by a 200 nm thick aluminum filter. The XUV probe pulse is then focused into the sample gas cell by a toroidal mirror, and the transmitted spectrum is dispersed by a concave grating and measured by an X-ray CCD camera. In this study, the photon energy range between 44 and 60 eV is mainly employed. The photon energies of the XUV spectrum are calibrated using well-known Fano resonances of neon between 40 and 50 eV [35,38]. By focusing the few-cycle NIR pulses into a quasi-static gas cell filled with argon, the transmitted spectrum is dispersed by a concave grating and measured by an X-ray CCD camera. In this study, the photon energy range between 44 and 60 eV is mainly employed. The photon energies of the XUV spectrum are calibrated using well-known Fano resonances of neon between 40 and 50 eV [35,38].

Discussion

Conical intersection dynamics in the alkyl iodides have long been a prototype for understanding nonadiabatic processes in photochemistry. In this work, nonadiabatic fragmentation dynamics of i-C₃H₇I and t-C₄H₉I are revealed by ultrafast XUV transient absorption spectroscopy. In both molecules, spectroscopic measurements from the perspective of core-to-valence excitations localized on iodine allow for a complete mapping of the chemical reaction from UV photoexcitation to photoproduct formation. The sensitive detection of transient molecular and atomic electronic states involved in the fragmentation pathway provides an exacting picture of ultrafast wave packet bifurcation between electronic states at a conical intersection. Specifically, XUV signatures portraying the cases of partial wave packet transfer in i-C₃H₇I leading to an intermediate I²⁺ branching ratio and nearly-complete wave packet transfer in t-C₄H₉I leading to the dominant formation of I atoms are captured. Furthermore, by comparisons to calculated spectra of a CH₃I model system, the XUV signatures are shown to be readily interpretable within a straightforward, one-electron picture of core-to-valence transitions.

The present study demonstrates the general advantages of resonant photoexcitation combined with a direct probing of valence electronic structure in the XUV for capturing non-adiabatic electronic state-switching in polyatomic systems. Future experiments with shorter pump pulses, achieving faster temporal resolution, will allow time-resolved constraints for the passage of i-C₃H₇I through the conical intersection to be more precisely characterized and compared to t-C₄H₉I, providing further insight into the influence of alkyl group structure on state-switching dynamics. In addition, complementary experiments probing core-level transitions at the carbon K-edge [10,11,44] could allow for the detection of structural dynamics within the R-group moiety of the alkyl iodides during C–I dissociation, thus providing a multi-dimensional picture of passage through the conical intersection.
Following this methodology, an instrument response function of $50 \pm 7$ fs is determined. Based on this, the UV pump pulses are anticipated to be $\approx 50$ fs in duration at the gas target.

Each time-dependent XUV spectrum of the i-C$_3$H$_4$H$_1$ experiment (Fig. 2a, c) and r-C$_3$H$_4$H$_5$ experiment (Fig. 2b, d) is obtained from an average of 70 and 50 X-ray camera frames, respectively. Each frame is captured at an integration time of 1 second per frame, 1000 laser pulses per second. In both experiments, XUV spectra are collected at time delays from $-50$ to 160 fs. Between $-20$ and 100 fs time delays, spectra are recorded at 4 fs intervals. Outside of this delay window (i.e., $-50$ to $-20$ fs and 100 to 160 fs), spectra are recorded at 10 fs intervals. The average standard deviation in AOCD across the 44–60 eV photon energy range of interest in the XUV spectrum is $\sigma_{\text{AOCD}} = 2$ mOD and is interpreted as the noise level of the experiments.

**Simulation details.** The simulations used to produce theoretical CH$_3$I transients for comparison to the experimental i-C$_3$H$_4$H$_1$ and t-C$_3$H$_4$H$_5$ results are published$^{37}$. In the simulations, nonadiabatic dynamics of CH$_3$I after photoexcitation to the $^3$Q$_0$ state were computed using Tully’s fewest-switches surface hopping theory implemented in the SHARC software package. The resulting molecular dynamics trajectory data were used for the computation of XUV transient absorption spectra simulated with OpenMolas using the MS-CASPT2 method and ANO-RCC-VTZP basis set. Molecular trajectories leading to the dissociation of I$^*$ and I atoms provide distinct signatures in the XUV transients, which are plotted in Supplementary Fig. 7. The methyl CH$_3$I transients shown in Fig. 2f are produced from direct sums of the XUV transients associated with I$^*$ and I dissociation, and with a Gaussian time-broadening applied (Supplementary Fig. 8, Note 6).

**Data availability**
The data supporting the findings of this study are available from the corresponding author upon reasonable request.

**Code availability**
The codes used to simulate the modified CH$_3$I transients and analyze the experimental results are available from the corresponding author upon reasonable request.

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Author contributions

K.F.C., D.M.N., and S.R.L. conceived the experiments. K.F.C. performed the experimental measurements and analyzed the results. M.R. and K.F.C. constructed the experimental pump pulse setup. H.W. and D.P. performed the theoretical calculations. K.F.C., D.M.N., and S.R.L. wrote the paper with inputs from M.R., H.W., S.M.P., Y.K., L.B., and D.P.

Competing Interests

The authors declare no competing interests.

Additional information

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