Deciphering methylation effects on $S_2(\pi\pi^*)$
internal conversion in the simplest linear
$\alpha,\beta$-unsaturated carbonyl

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Abstract

Chemical substituents can influence photodynamics by altering the location of critical points and topography of the potential energy surface (electronic effect) and by selectively altering the inertia of specific nuclear modes (inertial effects). Using non-adiabatic dynamics simulations, we investigate the impact of methylation on $S_2(\pi\pi^*)$ internal conversion in acrolein — the simplest linear $\alpha,\beta$-unsaturated carbonyl. Consistent with time constants reported in a previous time-resolved photoelectron spectroscopy study, $S_2/S_1$-deactivation occurs on an ultrafast timescale ($\sim$50 fs). However, our simulations do not corroborate the sequential decay model used to fit the experiment. Instead, upon reaching the $S_1$ state, the wavepacket bifurcates: a portion undergoes ballistic $S_1/S_0$-deactivation ($\sim$80 fs) mediated by fast bond-length alternation motion, while the remaining decays on the ps-timescale in a more statistical regime. Our analysis reveals that methyl substitution, generally assumed to mainly exert inertial influence, also manifests in important electronic effects due to its weak electron-donating ability. While methylation at the $\beta$ C-atom gives rise to effects principally of inertial nature,
such as retarding the twisting motion of the terminal $-\text{CHCH}_3$ group and increasing its coupling with pyramidalization, methylation at the $\alpha$ or carbonyl C-atom modifies the potential energy surfaces in a way that also contributes to altering the late $S_1$-decay behavior. Specifically, our results suggest that the factor-of-two slowing of the ps-component upon $\alpha$-methylation is a consequence of a tighter surface and reduced amplitude along the central pyramidalization, effectively restricting the access to the $S_1/S_0$-intersection seam. Our work offers new insight into the $S_2(\pi\pi^*)$ internal conversion mechanisms in acrolein and its methylated derivatives and highlights site-selective methylation as a tuning knob to manipulate photochemical reactions.

1 Introduction

Photoexcited dynamics of polyatomic molecules are of significant interest in a multitude of natural processes, such as vision, light-harvesting and photostability of DNA/RNA nucleobases. In the vicinity of conical intersections, the non-adiabatic coupling becomes significant, driving transitions between electronic states. Chemical substituents can drastically affect such non-adiabatic dynamics. Schuurman and Stolow have separated substituent effects into electronic and inertial components. The former accounts for the imprints on the electronic structure, i.e., changes in the location of critical points and topography of the potential energy surfaces (PESs), whereas the latter refers to changes in the inertia of specific nuclear modes that will affect the direction and velocity of the wavepacket on the PESs. The intricate details of how these effects play their part in the non-adiabatic dynamics are not obvious.

Schuurman, Stolow and coworkers have adopted a systematic approach combining time-resolved photo-electron spectroscopy (TRPES) with electronic-structure calculations (and recently, $ab$ initio non-adiabatic dynamics simulations) to study substituent effects on excited-state dynamics, focusing on unsaturated hydrocarbons. Introducing a methyl group at different positions of unsaturated hydrocarbons is expected to cause specific inertial ef-
fects. In allenes, increasing methylation at the terminal C-atom gradually slows down the twisting motion. This leads to a faster and unconstrained bending motion of the main allene moiety, modifying the pathway of excited-state deactivation.\textsuperscript{15} In cyclopentadienes, an increase in the inertia at the C5-position slows down the dynamics on $S_1$ by inhibiting the out-of-plane vibration at that center.\textsuperscript{14}

Another interesting class of unsaturated hydrocarbons is the $\alpha, \beta$-unsaturated carbonyls. Acrolein (AC) is the simplest example with its s-trans form (see Figure 1) being the most stable conformer at room temperature.\textsuperscript{24–28} Its multifunctional nature has made it a prototype molecule for studying photoexcitation involving both $n\pi^*$ and $\pi\pi^*$ excited-states.\textsuperscript{25,26,29–42} Methylation at the $\alpha$, $\beta$ and carbonyl C-atoms of AC can be expected to slow down important nuclear motions associated with internal conversion dynamics. Lee et al. combined femtosecond TRPES and static electronic-structure calculations to investigate methylation effects on $S_2(\pi\pi^*)$ photodynamics of AC, i.e., considering the methylated derivatives: crotonaldehyde (CR), methylvinylketone (MVK), and methacrolein (MA) (see Figure 1).\textsuperscript{22} Their study demonstrated distinct methylation effects in the experimental timescale interpreted to be associated with $S_1$ decay. This timescale was found to be significantly faster for CR but almost a factor-of-two slower for MA. Static electronic structure calculations and first-order branching space analyses were not enough to explain the origin of these differences. In the absence of dynamical simulations, it was conjectured that specific inertial effects are playing major roles in accelerating and decelerating dynamics near the intersection seams. In CR, it was speculated that the wavepacket might spend more time near the $S_1/S_0$-intersection seam because of a retarded torsional motion of the terminal $-\text{CHCH}_3$ group, resulting in faster $S_1$ decay. On the other hand, in MA, central methylation was proposed to slow down the non-adiabatic coupling vector dominated by this mode, leading to a less efficient and hence slower decay. Recently, the faster TRPES behavior of CR was reinterpreted in a multi-mode picture.\textsuperscript{43} Specifically, the efficient non-adiabatic transfer in CR was rationalized on the basis of a strong coupling (due to lack of symmetry at the conical intersection) between the
torsion and β C-atom pyramidalization modes at that intersection. However, these theory-based hypotheses have, to the best of our knowledge, never been examined from a dynamical perspective.

Furthermore, a recent study on the photexcited dynamics of methylated butadienes highlighted the importance of electronic effects of the weakly electron-donating methyl group, influencing non-radiative decay timescales and branching ratios. Electronic effects of the methylation have also been found to accelerate the photoisomerization of a methylated derivative of all-trans retinal (methylated at C10 position) in solution. In light of such developments, we aim to resolve the mechanistic details of S\textsubscript{2}(\pi\pi^*) internal conversion in AC and the role of inertial and electronic effects in its methylated derivatives using non-adiabatic dynamics simulations.

AC and its methylated derivatives are all present in the atmosphere as volatile organic compounds, being both the precursors and intermediates in several chemical processes, and thus, of significant photochemical interest. Despite the small size, characterizing the electronic structure of their excited-states have proven challenging. Early experimental study on AC from Walsh assigned absorption bands at 412, 387 and 193.5 nm to S\textsubscript{0}→T\textsubscript{1}(n\pi^*), S\textsubscript{0}→S\textsubscript{1}(n\pi^*) and S\textsubscript{0}→S\textsubscript{2}(\pi\pi^*) transitions, respectively. In addition, Birge and Leermakers assigned S\textsubscript{0}→S\textsubscript{1}(n\pi^*) and S\textsubscript{0}→T\textsubscript{1}(n\pi^*) transitions using vibrational electronic spectroscopy along with molecular orbital and spin-orbit coupling calculations for the methylated analogs of AC. Substantial attention has been devoted to S\textsubscript{1}(n\pi^*) photodynamics of AC, accessible through UV-A radiation, with focus on relaxation, isomerization and dissociation pathways. As such, the S\textsubscript{1}, T\textsubscript{1} and T\textsubscript{2} states of AC have been characterized both experimentally and theoretically, and they agree well. On the other hand, the character and vertical excitation energy of the S\textsubscript{2}(\pi\pi^*) state of AC have been a contentious topic. Moreover, to our knowledge, there is, no experimental study conclusively characterizing the S\textsubscript{0}→S\textsubscript{2} transition for CR, MVK and MA. Several theoretical studies have found S\textsubscript{0}→S\textsubscript{2} excitation energies of AC that overestimate the experimental values by ∼1 eV. This has
been attributed to the double-excited character and unresolved mixing between valence and Rydberg states at the Franck–Condon (FC) region. Using the multistate complete active space second-order perturbation theory (MS-CASPT2) and specially designed active space and basis sets, Aquilante et al. were able to characterize the S\(_2\) state of AC as a valence \(\pi\pi^*\) excitation. They also showed that S\(_1\) through S\(_3\) \((n\pi^*)\) are the only valence states below the Rydberg states. Since then, several theoretical studies have characterized the S\(_2\) state of AC at FC point employing high-level theories.

\[\text{Figure 1: Molecular structures of s-trans acrolein (AC), crotonaldehyde (CR), methylvinylketone (MVK) and methacrolein (MA).}\]

Experimentally, photoexcitation (~193 nm) to the S\(_2\) state of AC has predominantly been pursued to investigate photodissociation and photofragment formation. However, the photochemical details of the internal conversion dynamics following photoexcitation to the S\(_2\) state and the characterization of the conical intersections for nonradiative relaxation has received much less attention. Recently, non-adiabatic \textit{ab initio} multiple spawning (AIMS) simulations (employing hole-hole Tamm-Dancoff-approximated \((hh\text{-TDA})\) density functional theory) have been performed for AC initiated from the S\(_2\) excited-state for the prediction of time-resolved near edge X-ray absorption fine structure spectrum. Nonetheless, the mechanistic details have not been investigated yet.

In this work, we aim to decipher the mechanistic details of the internal conversion dynamics in AC initiated on S\(_2\)\((\pi\pi^*)\) and investigate inertial and electronic effects of methylation. We tackle this by performing and analyzing \(hh\text{-TDA}\) AIMS dynamics simulations across AC
and its methylated derivatives. Our resulting dynamical picture provides new insights into the mechanisms underlying the timescales associated with the previous TRPES measurements.\textsuperscript{22}

\section{Computational Methods}

To investigate the effects of methylation in the $\alpha,\beta$-unsaturated carbonyls, we employed $hh$-TDA method which includes both static and dynamical correlations efficiently. In this method, the starting point is an (N+2) electron reference state, and the ground- and excited-state wave functions are constructed by applying a pair of annihilation operators, which allows for a proper description of excited electronic states characterized by transitions into the lowest unoccupied molecular orbital. Unlike time-dependent density functional theory,\textsuperscript{72} this method can also describe the ground- and the excited-states on an equal footing, allowing for the correct description of the conical intersections between them. All $hh$-TDA calculations employed the 6-31G(d,p) basis set,\textsuperscript{73–75} and the $\omega$PBE\textsuperscript{76} exchange-correlational functional, with a range separation parameter of 0.3 Bohr$^{-1}$ and short-range Hartree–Fock exchange scaled by 0.3 a.u.. In a previous study, these parameters were found to produce relative energetics of the $S_0$ through $S_2$ states that compare favorably with higher-level electronic-structure methods.\textsuperscript{71} Here, we extend this benchmark to consider both relative energies and geometries at selected critical points by comparing to extended multistate complete active space second-order perturbation theory (XMS-CASPT2).\textsuperscript{56,77,78} Further details on the reference calculations and a discussion of benchmark are provided in Section S1 of the Supporting Information (SI). In short, we find an overall good agreement between $hh$-TDA and XMS-CASPT2.

Initial conditions (ICs) (i.e., coordinates and velocities) for computing absorption spectra and AIMS simulations were generated by sampling the ground-state harmonic Wigner distribution at 300 K. A total of 5000 ICs were randomly sampled for each molecule and
vertical transition energies and oscillator strengths were calculated. The resulting stick spectra were convolved with a Gaussian line shape (FWHM=0.2 eV) and uniformly red-shifted to match the first experimental absorption maximum\(^2\)\(^7\)\(^9\) (Figure S7) for each system. To approximately mimic a typical pump pulse width, ICs for the dynamics simulations were selected from a narrow window of 0.05 eV around 200 nm (6.20 eV) wavelength. The pump wavelength matches that in the second set of TRPES measurements by Lee et al. (pump: 200 nm, probe: 267 nm).\(^2\)\(^2\) Out of those ICs, we randomly selected 50 (60 for CR) of them, for each molecule, to start AIMS dynamics within the independent-first-generation approximation.\(^8\)\(^0\) Note that ten additional ICs were sampled for CR to ensure that the observed stalling of population decay around 600–900 fs (see below) was not due to undersampling. The simulations were initiated on \(S_2\) and propagated for 1 ps. The equations of motion were integrated using an adaptive time step of 20 a.u. (\(\sim 0.48\) fs), which was reduced upon encounter of non-adiabatic coupling regions. A coupling threshold of 0.005 \(E_h/\hbar\) (scalar product between derivative coupling and nuclear velocity vectors at a given time step) was employed for a trajectory basis function (TBF) to enter and exit a spawning region. TBFs were removed from the simulations when their population fell below 0.01. Furthermore, TBFs on the ground-state that did not couple with other TBFs for at least 5 fs were decoupled and terminated. Afterwards, the population of such TBFs were considered as contributing to the \(S_0\) population. Bootstrapping with 1500 samples was used to provide error estimates for the simulated decay time constants. All \(hh\)-TDA simulations were performed using the TeraChem package.\(^8\)\(^1\)\(^8\)\(^4\) Geometry optimizations and minimum energy conical intersection (MECI) searches were performed using the DL-FIND library\(^8\)\(^5\) interfaced with TeraChem. The XMS-CASPT2 calculations were performed using BAGEL.\(^8\)\(^6\)\(^8\)\(^7\)
3 Results and Discussion

Before discussing the dynamical results, we briefly consider key critical points characterizing PESs of the four $\alpha,\beta$-unsaturated carbonyls. A more detailed discussion is provided in Section S4. The dominant coordinates differentiating these points are terminal torsion (−CH$_2$ or −CHCH$_3$ in CR), bond-length alternation (BLA), pyramidalization of the terminal ($\beta$) or central ($\alpha$) C-atom (PyrT or PyrC, respectively) and changes in the central backbone angle (labeled by C, N and W to indicate contracted, neutral and wide angles, respectively). Definitions of geometric parameters are given in Figure S2 and Section S3.

Figure 2 summarizes the energetics of selected critical points obtained at the $hh$-TDA level. At the FC point, all systems exhibit similar planar configurations (ignoring methyl H-atoms) and energies for the three lowest singlet states. Methylation induces a 0.1–0.2 eV red-shift of the $S_2$ energies (most pronounced for MA), consistent with, albeit less pronounced than, the trend in the experimental absorption maxima (MA<CR<MVK<AC). The $S_2$/S$_1$-intersection seam is energetically accessible from the FC point: the lower-energy region of the seam is $\sim$2 eV below and predominantly features torsion and PyrC (CC$_{pyr}$ and/or WC$_{pyr}$ for contracted and wide angles, respectively) or torsion with limited pyramidalization (N) in CR (Section S4). In addition, we find a higher-energy terminal twist-pyramidalized MECI (NT$_{pyr}$). Analogous to the sudden polarization observed at twist-pyramidalized configurations in ethylene and butadiene, the $S_2$/S$_1$-intersections feature charge-transfer character across the ethylenic unit, with polarization direction governed by the dominating pyramidalization center. Due to its weakly electron-donating character through hyperconjugation, we expect different methylation sites to preferentially stabilize/destabilize certain configurations. In particular, terminal methylation in CR destabilizes $S_2$/S$_1$-MECI-NT$_{pyr}$ by $\sim$0.4 eV relative to the other systems. The $S_1$-minimum ($S_1$-min) is also planar but with a largely inverted BLA with respect to the FC point. The $S_1$/S$_0$-intersection seam is located energetically above the minimum, and reaching the lowest-energy $S_1$/S$_0$-MECI-N requires torsion and further BLA expansion. This MECI exhibits biradicaloid character.
with an unpaired electron residing on each of the orthogonal $n_O$ and terminal C-atom $2p$ orbitals. Methylation at the carbonyl C-atom (termed formyl methylation from hereafter) (i.e. in MVK) stabilizes this region of the seam, as the weakly electron-donating methyl group effectively compensates the partial positive charge on the carbonyl C-atom. This reduces the energy gap between the $S_1$-min and $S_1/S_0$-MECI-N from $\sim$0.7 (AC/CR/MA) to $\sim$0.4 eV (MVK). This electronic effect of methylation could affect ground-state recovery through internal conversion from $S_1$. However, our focus on $S_2$ photoexcitation implies that the wavepacket is vibrationally hot upon reaching $S_1$-min (gaining $>3$ eV additional kinetic energy), which could render the lower-energy regions of the seam less important. These aspects will be discussed further below.
Figure 2: Relative potential energies of important critical points for the four systems relative to their respective S\textsubscript{0}-minimum. Insets indicate the dominant valence structures (AC: R\textsubscript{1,2,3}=H; CR: R\textsubscript{1,2}=H, R\textsubscript{3}=CH\textsubscript{3}; MVK: R\textsubscript{2,3}=H, R\textsubscript{1}=CH\textsubscript{3}; MA: R\textsubscript{1,3}=H, R\textsubscript{2}=CH\textsubscript{3}). Although energies at the S\textsubscript{0}-min and S\textsubscript{1}-min are similar across all the molecules, the terminal twist-pyramidalized MECIs (NT\textsubscript{pyr}) are destabilized in CR, while S\textsubscript{1}/S\textsubscript{0}-MECI-N is stabilized by the formyl methylation in MVK.

Figure 3 presents the adiabatic population decay profiles obtained from the hh-TDA AIMS simulations. Following a short lagtime (∼25 fs), the population on S\textsubscript{2} decays on an ultrafast timescale to S\textsubscript{1}, whose growth is accompanied by a comparably fast ground-state recovery. The maximum in S\textsubscript{1} population (0.4–0.5) is reached at ∼200 fs, after which it decreases slowly. The fast-growth/slow-decay S\textsubscript{1} profile (or two distinct components of S\textsubscript{0} growth), combined with an intermediate max-population is not reminiscent of a sequential kinetic model (X→A→I→P) used in the TRPES study by Lee et al\textsuperscript{22} Rather, it signifies that the ground-state recovery occurs on two different timescales. We fitted the S\textsubscript{2} and S\textsubscript{0}
population profiles to delayed mono- and bi-exponential decays, respectively (see inset figures and Section S5). For the S$_2$ profiles, this yields time constants of $\sim$50 fs for AC/CR/MA and a slightly longer ($\sim$60 fs) for MVK. Fitting the S$_0$ repopulation yields an ultrafast time constant ($\sim$80 fs), as well as a longer ps-component. In CR, the ultrafast component dominates with $\sim$70% amplitude, whereas the two components have equal amplitudes in MA (AC/MVK are intermediate). The time constants for the long S$_1$ decay are comparable across AC/CR/MVK ($\sim$1 ps) but a factor-of-two larger in MA. Based on their TRPES-fitted sequential model, Lee et al. reported a similarly longer time constant for MA, but also a distinctly shorter for CR ($\sim$500 fs) compared to AC and MVK. In the following, we investigate the dynamical features underlying the population traces from our simulations and examine the role of inertial and electronic methylation effects at different positions in AC. Finally, we compare our findings with the original rationalization of the TRPES differences.
Figure 3: Population dynamics following excitation to the S\textsubscript{2}(\pi\pi^*) state as obtained from the \textit{hh}-TDA-\omega\textit{PBEh}/6-31G(d,p) AIMS simulations. Shaded regions mark one bootstrap standard deviation obtained from 1500 samples. Black dashed lines show fits (see also Section S5). The inset figures summarize the associated time constants (fs) and amplitudes obtained from the fits to the S\textsubscript{2} and S\textsubscript{0} profiles. The dashed arrow and dashed-outlined S\textsubscript{1} box indicate the portion of the wavepacket that escapes ballistic decay and proceeds to a more statistical regime (see text). The larger S\textsubscript{1} build-up in MA results from a combination of three factors: (i) its fast S\textsubscript{2}/S\textsubscript{1} decay; (ii) the slightly delayed onset of its S\textsubscript{1}/S\textsubscript{0} decay; and (iii) a comparatively smaller fraction of the S\textsubscript{1} wavepacket that undergoes decay in the ballistic regime.
Figure 4: Effect of methylation on the approach to the $S_2/S_1$-intersection seam. Time evolution of the $S_2$ density along the torsional mode within the first 300 fs following photoexcitation. The green crosses indicate the first non-adiabatic transfer event for each IC while the blue filled circles indicate subsequent transfer events following photoexcitation. In CR, non-adiabatic transfer events are encountered earlier along the torsion.
Figure 5: Departure from the FC point. Early time evolution (see color bar) of the centroids of the TBFs on $S_2$ in the subspace spanned by (left panel) PyrC and torsional modes, and (right panel) PyrT and torsional modes. The green crosses indicate the first non-adiabatic transfer event for each IC while the blue filled circles indicate subsequent transfer events within the first 150 fs following photoexcitation.

Figures 4 and S15 show the initial 300 fs time evolution of the $S_2$ wavepacket density along the torsional and BLA modes, respectively. The green crosses indicate the first non-
adiabatic transfer event for each IC while subsequent events are marked by blue filled circles. Consistent with previous studies on AC, departure from the FC region is initiated by ultrafast BLA expansion and then proceeds along the torsion. This brings the systems in proximity to the S$_2$/S$_1$-intersection seam, marking the onset of population decay. Figure 4 already demonstrates effects of methylation: (i) the torsional motion is slowed down in CR. This is expected from the higher torsional inertia imposed by the heavier methyl group that, in turn, slightly delays the onset of population decay; (ii) in AC/MVK/MA, the wavepacket significantly overshoots 90°-torsional configurations following the initial approach to the intersection seam. Such large-amplitude torsional motion is absent in CR; and (iii) for MVK, a small portion of the wavepacket is transiently trapped around planar configurations. This gives rise to the observed tail in the S$_2$ population decay and the slightly longer S$_2$ decay time (Figure 3). To understand these differences, we consider the additional modes activated during the early dynamics.

Figure 5 illustrates the early time evolution (<150 fs) of the centroids of the TBFs on S$_2$ in the subspace spanned by the torsional and the PyrT or PyrC modes. There is no clear correlation between PyrT and torsion in AC/MVK/MA, where substantial pyramidalization mostly ensues near ~90°-twisted configurations. On the other hand, the extent and direction of PyrC are clearly coupled to the torsional mode at twisted configurations. In CR, such correlation exists for both PyrT/PyrC, and it emerges already as the wavepacket leaves the FC region. The directed PyrT motion results from the asymmetric mass distribution at the terminal C-atom, implying retarded torsion of the methyl group relative to the H-atom. Consequently, the torsion direction dictates the PyrT direction, and the PyrC motion necessarily counter-rotates to conserve total angular momentum. This correlated motion manifests in a somewhat different decay behavior for CR, as will be discussed further below.

As seen from the location of the first and subsequent non-adiabatic transitions in Figure 5 (green crosses and blue filled circles, respectively), the (un)correlated PyrT/PyrC and torsion trends also characterize the accessed part of the intersection seam. When we consider the
(PyrC, PyrT)-distributions of all S$_2$/S$_1$ non-adiabatic transfer events (Figure 6), additional differences become clear. The black markers indicate the position of the optimized MECIs in the positive quadrant. Near-degenerate MECIs also exist (not shown) in other quadrants with all possible positive and negative combinations of PyrT and PyrC values. For MA, the non-adiabatic transfer occurs primarily at highly terminally pyramidalized geometries (|PyrT| > 20°) and intermediate central angles (see coloring), i.e., mostly near MECI-NT$_{pyr}$.

A similar picture emerges for MVK, but with a larger spread in PyrC, as expected due to the lack of the central methyl group to restrict the motion. Yet, by comparing to AC, it is clear that methylation at the carbonyl C-atom does impose additional constraints, influencing the accessed intersection seam. As such, AC explores both highly terminally and centrally pyramidalized geometries. It should be noted that the tighter PyrC behavior in MA is not only a result of increased inertia of the central methyl group but also due to electronic effects, as seen from a comparison between the S$_2$ PES PyrC-torsion cuts around S$_2$/S$_1$-MECI-NT$_{pyr}$ for AC and MA (Figure S13). For CR, this region of the intersection seam is dynamically inaccessible. Rather, the correlated PyrT/PyrC and torsional motion initially guides the wavepacket toward a part of the intersection seam characterized by lower torsion (<75°) and simultaneous PyrT and PyrC (green crosses and black-outlined circles in Figures 5 and 6, respectively). MECI searches starting from the associated non-adiabatic transitions end in S$_2$/S$_1$-MECI-NT$_{pyr}$, indicating that CR accesses a higher-lying, non-stationary part of the intersection seam earlier in the dynamics. As the system approaches 90°-twisted structures, the extent of PyrT is reduced. As will be discussed later, this coordinated motion upon reaching S$_1$ also promotes initial ground-state recovery.

Next, we turn to point (ii), pertaining to the torsional overshooting in AC/MVK/MA. In line with the identified MECIs and the dynamics discussed above, reaching the intersection seam requires pyramidalization — motion that is primarily activated near 90°-twisted configurations in these three systems. Together with the initial ballistic torsional behavior, this results in a first passage through methylene 90°-twisted configurations, that does not
efficiently induce population transfer (see Figure S16). On the other hand, the combination of the correlated pyramidalization and torsional motion in CR steers the wavepacket toward the intersection seam already at partially twisted geometries, leading to substantial population decay earlier along the torsional mode.

While the timescale for $S_2$ relaxation is ultrafast across all systems, MVK exhibits a slightly slower decay. As alluded to in (iii) above, this results from a transient delay of the wavepacket around planar configurations. At the FC point, the wavepacket is directed downhill toward lower-energy regions ($\sim 0.7$ eV below the FC point), characterized by expanded BLA, thereby generating BLA oscillations. The search for a planar $S_2$ minimum from the FC point was unsuccessful in all molecules, leading to an imaginary frequency along the torsion. However, we located a shallow minimum (torsional barrier $<0.05$ eV as estimated by a nudged-elastic-band calculation connecting $S_2\text{-min}^*$ and $S_2/S_1$-MECI-WC$_{pyr}$) in MVK upon rotating the methyl group to align one of its H-atoms with a methylene H-atom (see $S_2\text{-min}^*$ in Figures S5 and S14). Note that we could not confirm similar structure to be a true minimum at the XMS-CASPT2 level (see Section S1 for additional details). While this could be a potential cause of transient trapping, inspection of the associated ICs in MVK indicates an alternative explanation. In particular, it suggests that the delay is induced by either an initial in-phase motion along the PyrT and PyrC modes or an overall swinging of the central C-atom. Importantly, these modes both hinder progress of methylene torsion and are imprinted already in the IC sampling. Indeed, comparing the normal modes across systems, we find two (instead of one) low-frequency in-phase modes in MVK (Figure S17). This suggests that the delay is of inertial origin rather than a consequence of a tiny potential barrier at the $hh$-TDA level. Having analyzed the ultrafast $S_2$ relaxation dynamics and how methylation impacts the departure of the wavepacket from the FC point, we next consider the mechanisms governing ground-state recovery.

The ultrafast ($\sim 80$-fs) and longer ($\sim 1$-ps) timescale components from our $S_0$ population fitting indicate that the ground-state recovery proceeds in two different regimes: (i) a ballistic
Figure 6: (PyrT, PyrC) distribution for all $S_2/S_1$ transition events. The area of each circle represents the absolute population transfer. Identified $S_2/S_1$-MECIs are indicated by black markers and their energies relative to the respective $S_0$-min are reported in eV. The first $S_2/S_1$ transition events for each IC are distinguished by black edge colors. The classification of the central angle into contracted (C), neutral (N) and wide (W) are indicated by the coloring. Vertical and horizontal dashed lines serve as guides for the eye.

regime in which the wavepacket is brought to the $S_1/S_0$-intersection seam before significant intramolecular vibrational redistribution (IVR) has occurred. In this limit, the direction and velocity of the wavepacket approach to the intersection seam become key variables dictating
the non-adiabatic dynamics, and (ii) a more statistical regime, where the wavepacket exists on S_1 for long enough to allow for significant IVR prior to the decay. Here, the access to the intersection seam is expected to be increasingly governed by relative energetics, although a high kinetic energy excess can distort this picture. According to the fit amplitudes, the ultrafast decay accounts for 50-70% (AC: 60%, CR: 66%, MVK: 59%, and MA: 50%) of the ground-state recovery with the remaining population transferring in the more statistical regime. Importantly, while the ultrafast S_0 population growth is largely comparable across systems, the longer time constant is about twice as long in MA. Below, we divide the decay into early and late time bins (fast: 0-120 and slow: >120 fs) to facilitate further analysis of the dynamical behavior in these two regimes. This 120-fs threshold corresponds approximately to the time at which ~60% of the ultrafast repopulation has taken place.

To elucidate the mechanistic details underlying the ultrafast time constant of S_0 repopulation, we examined the geometric displacements necessary to bring the wavepacket from the S_2/S_1-intersection seam to the regions of the S_1/S_0 seam accessed at early times. Figure 7 displays the population-transfer-weighted PyrT and BLA distributions of the S_1/S_0 non-adiabatic transfer events together with the S_2/S_1 counterparts. Additional geometric parameters are provided in Figures S19 and S20. The corresponding ∆BLA and ∆|PyrT| distributions representing the changes in going from the parent S_2/S_1 to the pertinent S_1/S_0 transfer event are shown in Figure S21. For the methylated derivatives, the early S_1 decay (red bars) is characterized by a reduction in the fast BLA mode (period time of ~25 fs). For MA and MVK, this change represents the main displacement required to reach the S_1/S_0 counterparts of MECI-NT_pyr, dominating the S_2/S_1 decay. Although CR does not access the terminal twist-pyramidalized part of the seam, the BLA-mediated picture remains the same. This behavior is less distinct for AC, as expected from its larger variation in the S_2/S_1 non-adiabatic transition characteristics (Figure 6). In other words, the early decay is facilitated by the geometric and energetic proximity of a higher-lying S_1/S_0-intersection seam, which can be reached quickly along the fast BLA mode prior to any substantial planarization of
the comparatively slower torsional mode (period: \(\sim 100\) fs (160 fs for CR)).

Beyond these similarities, there are notable differences in the relative importance of the ballistic component (\(\sim 20\%\) more prominent for CR than MA) that can all be linked to distinct dynamical behaviors. Terminal methylation promotes ballistic decay in three ways: (i) the coordinated PyrC and torsional motion directs the \(S_1\) wavepacket along the higher-lying part of the \(S_1/S_0\)-intersection seam immediately upon reaching \(S_1\) (see early time
evolution in SI movie); (ii) the slower torsional motion extends the time window in which ballistic transfer occurs (Figure S18); and (iii) the decay to S$_1$ at lower torsion and larger PyrC angles expands the accessed part of the seam. Altogether, these effects increase the population transfer (and efficiency) of the ballistic decay in CR (gray bar charts in Figure 8). Conversely, the central methylation in MA leads to a faster and more directional torsional motion toward the S$_2$/$S_1$-intersection seam (Figure S18) and hence upon reaching S$_1$. While this fast torsional motion accelerates S$_2$/S$_1$ decay, it impedes the ultrafast ground-state recovery by rapidly driving the wavepacket away from the S$_1$/S$_0$-intersection seam, instead causing initial torsional spinning (Figure 8 and SI movie). Together with the slightly delayed onset of the S$_1$/S$_0$ decay, this accounts for the larger build-up of S$_1$ population for MA in Figure 3. It should further be noted that the larger ballistic component in CR can explain the more pronounced bi-exponential decay behavior of its S$_1$ population profile relative to the mono-exponential decay behavior in MA (not fitted).
Figure 8: Torsional evolution (left axis) at the centroids of the TBFs on $S_1$. The line transparency is proportional to the squared amplitudes (i.e., an incoherent approximation for the TBF population). Non-adiabatic transitions to $S_0$ are indicated by blue filled circles with area scaled according to the absolute population transfer. The number of non-adiabatic transfer events in the early and late time bins are shown next to the vertical 120-fs threshold line. The bar charts at the bottom report the average transfer efficiency over time (right axis). The gray-shaded horizontal regions indicate dihedral spans $(2n+1)90^\circ \pm 10^\circ$ for integer $n$.

The portion of the wavepacket escaping non-adiabatic transfer in the ballistic regime (missing the seam or only partially transferring) proceeds primarily toward the planar $S_1$-
minimum. At that point, several factors can influence the subsequent decay to the ground-state: (i) any remaining non-statistical behavior; (ii) the energetic location of the S₁/S₀-intersection seams and their topographies; (iii) the number of degrees of freedom and hence the available energy per vibrational degree of freedom (assuming equipartitioning). Each of these factors will be sensitive to the methylation pattern: two immediate effects being the fewer degrees of freedom in AC, and the ~0.3 eV stabilization of the lowest-energy region of the S₁/S₀-intersection seam by the formyl methylation in MVK discussed earlier (Figure 2). Below, we explore the origins of the similarity in long timescale-component for ground-state recovery in AC/CR/MVK and the factor-of-two slowing in MA.

As shown in Figure 7 (blue bars), the geometries mediating the late S₁ decay display increased BLA and reduced PyrT values, i.e., changing the largely bimodal early PyrT distributions of AC/MVK/MA toward broad unimodal distributions centered around zero. These changes are characteristic of the lowest-energy S₁/S₀-MECI-N, which is indeed expected to be increasingly important in the more statistical regime. However, the excess kinetic energy (sum of average kinetic energy and energy gap between the FC point and S₁/S₀-MECI-N) causes vigorous motion and hence a broader distribution of configurations mediating population transfer. This will inevitably complicate any analysis based on lowest-energy MECIs, particularly for AC with its fewer vibrational degrees of freedom (implying an additional 0.05–0.07 eV excess kinetic energy per degree of freedom compared to the other systems). A comparison between the temporal distributions of the S₁/S₀ non-adiabatic transitions and their average transfer efficiency (Figures 8 and S22) shows that AC features up to twice as many events in the late time bin (120–1000 fs) as well as the lowest transfer efficiency among all systems. Thus, it is clear that the rather different behavior underlies the comparable long time constants in AC/CR/MVK: while it is easier to reach the S₁/S₀-intersection seam in AC, the approach to the seam renders population transfer less effective than in CR/MVK. In passing, we note that a plateau in the S₁/S₀ population profiles (between 600–900 fs) in CR (Figure S25) contributes to a slight slowing of its longer time constant relative to MVK. In
MA, the combination of fewer non-adiabatic transition events and relatively lower transfer efficiency (slightly higher than AC) is the source of the factor-of-two longer time constant.

Figure 9 shows the accumulated $S_1$ wavepacket density along the PyrC and torsional modes (orange contours) together with the distribution of $S_1/S_0$ non-adiabatic transitions (blue contours). The motion along PyrC on $S_1$ is much more restricted in MA. A similar trend is observed for the accessed intersection seam. Across systems, the seam is associated with correlated PyrC and torsional motion, particularly in MA. This is highlighted by the black lines in Figure 9 obtained from Deming regression of the non-adiabatic transitions located around 90°-torsion. Together with the tighter PyrC span, it means that the population transfer occurs over a narrower effective torsional range in MA than in the other systems (torsion span around 90° encompassing 75% of the transfer events is for AC: ±30°, CR: ±29°, MVK: ±33°, and MA: ±25°). Accordingly, this suggests that central pyramidalization limits the dynamical access to the $S_1/S_0$-MECI-N part of the intersection seam, governing the late decay. Indeed, quantifying the population transfer within a similarly restricted PyrC-torsional span in AC/CR/MVK yields values comparable to MA (Figure 10), supporting this picture. This analysis was done by defining a rectangle enclosing 75% of the >120 fs population transfer in MA, corresponding to ~87% along and orthogonal to the fitted black line in Figure 9 and then considering the population transfer in AC/CR/MVK within this restricted region.

To understand the origin of this central methylation effect, we compared two different $S_1$ PES cuts along the PyrC and torsional modes for AC and MA: a relaxed and an unrelaxed scan. In the latter, all geometric parameters, but PyrC and torsion, were fixed to their $S_1/S_0$-MECI-N values (Figure S26). Two effects emerge from these results: (i) a tightening of the $S_1$ potential along PyrC; and (ii) a larger opening of the $S_1/S_0$-energy gap upon relaxation, effectively bringing the system farther away from the intersection seam region. The main difference between $S_1/S_0$-MECI-N and the relaxed (PyrC, torsion)-counterpart is a ~10° widening of the $\angle C_2C_1O$ angle. Together with the lower kinetic energy per degree
of freedom (further contributing to smaller vibrational amplitudes), these effects appear to explain the more restricted access to the intersection seam in MA with respect to AC in spite of their comparable uphill $S_1/S_0$-MECI-N energetics (Figure 2).

Figure 9: Accumulated $S_1$ wavepacket density (orange contours) along the PyrC and torsional (wrapped) modes together with distribution of $S_1/S_0$ non-adiabatic transition events (blue contours, normalized for each molecule). While these two coordinates are largely uncorrelated on $S_1$, this is not the case at the non-adiabatic transitions. The accessed PyrC span is significantly smaller in MA than in the other systems. The red square indicates the angle distribution in which $\sim 75\%$ of the MA population is transferred. The black lines indicate the intersection seam, as obtained by the Deming regression of the non-adiabatic transfer events centered around $90^\circ$-torsion.

Figure 11 summarizes the main features of the non-adiabatic mechanisms emerging from our simulations. Following photoexcitation, the wavepacket proceeds predominantly toward a higher-lying terminal twist-pyramidalized $S_2/S_1$-intersection seam, characterized by charge-transfer across the ethylenic unit. This facilitates decay to $S_1$ on the $\sim 50$ fs timescale from which ground-state recovery proceeds along two almost equally important pathways: an early ballistic followed by a ps-timescale statistical channel. Initially, prior to any significant planarization, the wavepacket reaches a higher-energy $S_1/S_0$-intersection seam by fast BLA contraction. The charge-transfer character is preserved along this pathway. The
Figure 10: The total S\textsubscript{0} population profile (solid lines) together with the contribution transferring inside (dashed) the torsion-pyramidalization range defined by the red outlined rectangles in Figure 9. As evident, the "inside" population traces are largely comparable across systems as opposed to the total. This suggests that the main factor limiting the efficiency of the late, more statistical ground-state recovery in MA is a restricted access to the intersection seam.

Portion of the wavepacket escaping ballistic decay evolves toward the S\textsubscript{1}-minimum, where deactivation becomes increasingly statistical. It is dominated by torsional motion and BLA expansion (i.e., limited pyramidalization) as required to access the lowest-energy S\textsubscript{1}/S\textsubscript{0}-intersection seam. This pathway exhibits covalent character corresponding to biradicaloid species. However, it is important to note that the high excess kinetic energy upon reaching S\textsubscript{1} from S\textsubscript{2} leads to vigorous motion and hence a broader distribution of structures mediating population transfer. It should also be noted that the twist-pyramidalized MECIs of the \(\alpha, \beta\)-unsaturated carbonyls associated with charge-transfer character resemble those reported to mediate S\textsubscript{1}/S\textsubscript{0} decay in ethylene and butadiene.\textsuperscript{19,90,91,100–102} Conversely, the lowest-energy S\textsubscript{1}/S\textsubscript{0}-MECI-N exhibits a different covalent character (Section S4) from that reported to facilitate S\textsubscript{1}/S\textsubscript{0} transfer via the covalent pathway in butadiene.\textsuperscript{19,36,90,91} Ref. 43 provides an instructive overview.

The above general picture is affected by the methylation site. The terminal methylation in CR leads to a departure from the FC region that is notably different: torsion, PyrT, and
Figure 11: Schematic overview of the excited-state decay mechanisms as obtained from our AIMS simulations. Following $S_2$ photoexcitation, the wavepacket proceeds toward a terminal twist-pyramidalized intersection seam that mediates ultrafast decay on a $\sim 50$ fs timescale. Once on $S_1$, the wavepacket bifurcates: (i) more than 50% relaxes to $S_0$ in a ballistic regime through a geometrically-proximate $S_1/S_0$-intersection seam reached by ultrafast BLA contraction (blue arrows); (ii) the remainder wavepacket relaxes toward the BLA-inverted, planar $S_1$-minimum (green arrows). Ground-state recovery becomes increasingly statistical on the picosecond timescale primarily via twisted and non-pyramidalized configurations, as characteristic of the lower-energy $S_1/S_0$-intersection seam.

PyrC become correlated, and this correlated motion initially brings the wavepacket near a higher-lying part of the $S_2/S_1$-intersection seam, otherwise unexplored in the other systems. Conversely, the fast and uncorrelated torsional motion in AC/MVK/MA causes inefficient population transfer during the first passage near the $S_2/S_1$-intersection seam. Once on $S_1$, the ultrafast ballistic decay ensues predominantly along reduced BLA and the slower, more statistical decay occurs along expanded BLA for the methylated derivatives. Terminal methylation also exerts distinct effects on the $S_1$ decay. Specifically, the correlated torsional and pyramidalization motion initially guides the wavepacket along the $S_1/S_0$-intersection seam promoting ballistic decay in CR. The opposite is true for MA where a fast torsional
motion upon reaching $S_1$ rapidly removes the wavepacket from the seam. Central methylation in MA further slows down the decay in the statistical regime by restricting the access to the $S_1/S_0$-intersection seam. This can be attributed to a combination of two effects: (i) an electronic component causing a tightening of the PES along PyrC; and (ii) a thermal (as opposed to an inertial) component that contributes to a smaller PyrC amplitude in MA due to the lower gain in excess kinetic energy per degree of freedom upon reaching $S_1$-min relative to AC. In addition, formyl methylation leading to an enone (MVK) stabilizes the lowest energy $S_1/S_0$-MECI by $\sim 0.3$ eV compared to the other molecules. However, such electronic effect does not manifest critically in the $S_1/S_0$-deactivation following $S_2(\pi\pi^*)$ photoexcitation due to the large gain in excess kinetic energy upon reaching $S_1$.

Finally, we attempt to interpret the TRPES results by Lee et al.\textsuperscript{22} in light of the mechanistic details uncovered by our simulations. It should be noted that a strict theory–experiment comparison would require the explicit calculation of TRPES observables: the kinetic energy release in TRPES can shift due to energy stabilization/destabilization and changing state characters along the neutral and cationic pathways, implying that population traces and TRPES signals do not present a one-to-one mapping.\textsuperscript{103–107} Lee et al. used a four-component sequential kinetic model ($X \rightarrow A \rightarrow I \rightarrow P$) with the first component $X$ accounting for the instrument response function (IRF $\sim 160$ fs), and the remaining three corresponding to a sequential decay: an immediately excited species $A$ decays in an ultrafast manner to an intermediate $I$, which then decays to a product $P$ on the ps-timescale. The ultrafast time constant in this model was interpreted as the departure of the wavepacket from the FC region and the slower component as the ground-state recovery from $S_1$, possibly with some degree of intersystem crossing. While the ultrafast TPRES component is largely comparable across systems (50–190 fs), terminal and central methylation shortens and extends, respectively, the $S_1$ lifetime (AC: $\sim 620$; CR: $\sim 500$; MVK: $\sim 1040$; MA: $\sim 1800$ fs). Lee et al. rationalized these differences based on inertial effects and first-order branching space analyses of the lowest-energy MECI (labeled $S_1/S_0$-MECI-N in this work). The faster $S_1$
internal conversion in CR was proposed to originate from a slowing of the torsional motion (a seam coordinate in the linear approximation). This allows the wavepacket to stay near the intersection seam that is reached by BLA and PyrC displacements (dominating the gradient difference and non-adiabatic coupling vectors, respectively, Figure S28). Conversely, the central methyl group was conjectured to slow down motion along the PyrC-dominated non-adiabatic coupling vector, thereby reducing the effective coupling strength and, in turn, retarding the $S_1/S_0$ decay.

The picture emerging from our simulations differs in central ways yet supports parts of the proposed explanations. First, our results suggest a non-sequential model involving $S_1/S_0$ decay in both ballistic and statistical regimes with the former accounting for half or more of the decay. Second, while the simulations reproduce the factor-of-two slowing of the late $S_1$ decay in MA, the time constants are comparable across AC/CR/MVK (in contrast to the faster CR decay found experimentally). Besides the inherent limitations in the present theory–experiment comparison mentioned above, this difference may be explained by a combination of the sequential model assumed in the experimental fitting and the larger ultrafast ballistic component in CR (responsible for $\sim 70\%$ of the decay) suggested in this work. In other words, our results indicate that the main imprint of terminal methylation on the $S_1$ deactivation is to be found in the ballistic and not the statistical regime. However, the mechanism underlying the more pronounced ballistic decay aligns with the original rationalization. We find that terminal methylation induces correlated torsional-PyrC motion that upon reaching $S_1$ initially guides the wavepacket along a higher-lying part of the $S_1/S_0$-intersection seam. This increases the interaction time and, in turn, population transfer in the ballistic regime. Our dynamical picture for MA indicates that the slower ground-state recovery is the combined result of (i) an initial fast torsional motion that drives the system away from the higher-lying intersection seam accessed in the ballistic regime and (ii) a more limited access to the lower-lying intersection seam accessed at later times, thereby extending the longer decay constant. In other words, central methylation effects manifest mainly
through restricted seam accessibility due to a smaller PyrC amplitude rather than through a reduced transfer efficiency at the seam. Specifically, although the velocity component along the non-adiabatic coupling vector is smallest in MA, we see no clear correlation between the average population transfer and the velocity component along the non-adiabatic coupling vector in the statistical regime (comparing Figures S22 and S27). Pertaining to the time constants for $S_2$ relaxation, we find an overall good agreement with the ultrafast TRPES components. Although the differences are small in our simulations and within the IRF in the experiment, we reproduce the slower behavior in MVK and ascribe it to a small fraction of in-phase PyrC/PyrT motion out of the FC region, delaying torsional approach to the $S_2/S_1$-intersection seam.

An aspect not covered in the present work is the possibility of intersystem crossing from $S_1$ to the triplet manifold. Previous works indicate that triplet states are involved in the dynamics following $S_1(n\pi^*)$ photoexcitation due to their energetic proximity at the planar $S_1$-min and the energetically uphill approach to the $S_1/S_0$-intersection seam. Upon $S_2(\pi\pi^*)$ photoexcitation, intersystem crossing is, however, expected to be less prominent due to both the ballistic and hot statistical channels, which promote internal conversion to the ground-state. Yet some degree of intersystem crossing may be relevant for the longer-lived $S_1$ behavior. This was conjectured based on the HCO ground-state fragments detected during photolysis of AC and CR at 193 nm. However, the singlet/triplet branching ratios remain elusive. The longer $S_1$ lifetime of MA indicates that central methylation could make the system more prone to undergo intersystem crossing following $S_2(\pi\pi^*)$ photoexcitation. Future work considering the triplet manifold is required to resolve these questions.

4 Conclusion

We have investigated the impact of methylation on internal conversion dynamics of AC following photoexcitation to $S_2(\pi\pi^*)$. The main features of our simulations can be summarized
as follows. Following photoexcitation, the wavepacket undergoes ultrafast decay (∼50 fs) to S₁ from which ground-state recovery occurs in two different regimes: (i) ∼60% of the population decays in a ballistic regime mediated by ultrafast BLA motion; and (ii) the part escaping ballistic decay proceeds toward the planar S₁-min from which more statistical decay takes place on the ps-timescale. Although this general picture is largely preserved, methylation affects both timescales and underlying dynamical features.

Although methyl substitution is commonly assumed to exert inertial effects, its weakly electron-donating capacity can alter the energies and topographies of the PESs. Our simulations indicate that terminal methylation (β C-atom) mainly manifests through inertial effects: it leads to correlated torsional and pyramidalization motion that guides the wavepacket along the S₁/S₀-intersection seam, promoting decay in the ballistic regime for CR. On the other hand, central methylation (α C-atom) impedes ballistic decay by inducing fast torsional motion that brings the system away from the intersection seam. It further slows down deactivation in the statistical regime by a factor-of-two in line with previous TRPES time constants. However, according to our simulations this is a result of a restricted access to the intersection seam more so than an inefficient population transfer at the seam, as originally proposed. We attribute this to two factors: (i) an electronic component that tightens the PES along central pyramidalization; and (ii) a colder thermal component, which reduces the amplitude of the central pyramidalization. Electronic effects of methylation are also pronounced upon changing the system to an enone (MVK), leading to a ∼0.3 eV stabilization of the lower-energy S₁/S₀-intersection seam. However, the dynamical implications of this change are limited in the present case of S₂(ππ*) photoexcitation due to the large excess kinetic energy available upon reaching S₁.

The present study lays the foundation for future work focused on elucidating new and remaining mechanistic aspects. First, our simulations suggest a non-sequential S₁ decay as opposed to the sequential model assumed in the previous TRPES study by Lee et al. The timescale of the long S₀-repopulation trace for CR simulations does not follow the
accelerated TRPES trend obtained under this assumption. We find terminal methylation to promote decay in the ballistic rather than in the statistical regime. Addressing this aspect will require explicit calculation of TRPES observables and reconsideration of the fitting model in the experiment. Second, the longer $S_1$ time constant in MA suggests a potentially larger involvement of triplet states also in the dynamics initiated on $S_2$, requiring account of intersystem crossing in the simulations. Third, a different but related aspect pertains to the predicted electronic effects of formyl methylation. While the improved energetic access to the lowest-energy $S_1/S_0$-intersection seam in MVK does not significantly manifest in the present case, it could potentially have a pronounced impact on the singlet/triplet branching ratio following $S_1$ photoexcitation. We hope this work will stimulate further investigations to shed light on these questions.

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Supporting Information Available

Validation of $hh$-TDA against XMS-CASPT2, MECI nomenclature, geometric parameters and relative energies at critical point geometries, critical point analysis, adiabatic population fitting and additional supporting analyses are provided in the supporting information.

The following files are available free of charge.
• SI.pdf: Supplementary information

• SI_movie.mp4: Accumulated $S_1$ population along the PyrC or PyrT and torsional modes over time (red contours), together with the accumulated distribution of $S_1/S_0$ non-adiabatic transfer events (blue contours)

• https://doi.org/10.5281/zenodo.7780176: xyz files for critical points at the hh-TDA and XMS-CASPT2 levels of theory, input files for geometry optimization and MECI calculations, and initial conditions (positions and momenta) used in the AIMS dynamics.

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