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Unraveling the Structural Origins of Stimulated Emission Redshift in Cyanine Dye 1122C: A Combined AIMD and Machine Learning Study

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Abstract

1,1'-Diethyl-2,2'-cyanine (1122C) is known to undergo ultrafast *trans-cis* photoisomerization; however, its excited-state dynamics remain elusive. In this study, we present a comprehensive picture of the excited-state behavior of 1122C through ground-state structural exploration and excited-state reaction path calculations. We then performed excited-state dynamics simulations and used the results to reproduce the stimulated emission (SE) spectrum theoretically. The calculated spectral changes showed qualitative agreement with experimental observations. To further elucidate the driving forces behind the spectral changes, we employed machine learning to uncover key structural deformations correlated with SE redshift. This integrated approach provides new mechanistic insight into the ultrafast dynamics of cyanine dyes and demonstrates the utility of data-driven analysis in interpreting complex excited-state processes.

1. Introduction

Trans-cis photoisomerization is a light-induced chemical reaction triggered by irradiation in the visible to ultraviolet region. This process has attracted considerable attention not only in materials science – for example, in photoswitches and molecular motors,^{1,2} – but also in biological systems, such as the photoisomerization of the retinal chromophore in rhodopsin, which is essential for vision.^{3,4} Photochemical systems are typically characterized by carbon-carbon or nitrogen-nitrogen double bonds at their functional centers. As a result, molecules such as stilbene and azobenzene have been widely studied as model systems for *trans-cis* photoisomerization,^{5–8} and their excited-state dynamics have been extensively investigated using both experimental and theoretical approaches.^{9–22}

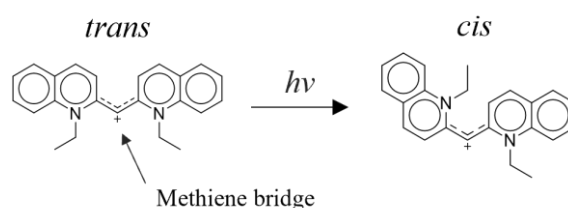


Figure 1. *Trans-cis* photoisomerization of 1,1'-diethyl-2,2'-cyanin (1122C). The molecule has a central methine bridge conjugated with aromatic rings at both termini.

1,1'-diethyl-2,2'-cyanine (1122C) is a dye molecule known to undergo *trans-cis* photoisomerization *via* torsional motion of its central methine chain (**Figure 1**). Dietzek *et al.* conducted transient absorption and stimulated emission (SE) spectroscopy experiments on 1122C.^{23–26} SE occurs when an excited molecule is induced to return to the ground state through interaction with incident light. The wavelength of SE, therefore, corresponds to the energy gap between the S_1 and S_0 states. Based on the observed SE signals, it was proposed that following vertical excitation, the 1122C ensemble undergoes barrierless *trans-cis* photoisomerization on the excited-state potential energy surface (PES) within 250–800 fs, and subsequently remains near

the bottom of the excited-state PES for 3.5–4.9 ps without deactivation to the ground state.²⁶ While such transient absorption experiments provide valuable insight into the excited-state dynamics of 1122C, they cannot directly capture the molecular structural changes governed by the topology of the PES. To interpret these spectroscopic observations at the atomistic level, many studies have examined the one-dimensional potential energy curve along the torsional angle of the methine chain, which is primarily associated with *trans-cis* photoisomerization. However, this choice of coordinate is heavily based on chemical intuition, and it remains uncertain whether a single torsional angle alone can sufficiently describe the excited-state dynamics of the 1122C ensemble.

To address this, we have developed the Reaction Space Projector (ReSPer) method,^{27–30} which extracts principal coordinates from reference structures using dimensionality reduction techniques. We previously applied ReSPer to the photoisomerization of *cis*-stilbene,³⁰ where we visualized a two-dimensional reaction space defined by two principal coordinates that implicitly included the central C=C torsion angle. This framework enabled the construction of a multi-state energy landscape that captured structural changes during the photoreaction and deactivation of *cis*-stilbene.³⁰ In recent years, unsupervised machine learning has also been applied to nonadiabatic molecular dynamics simulations. Zhu *et al.* developed a method combining dimensionality reduction with clustering to classify nonadiabatic transition structures into distinct reaction channels.³¹ This enables automatic extraction of important reaction coordinates without manual inspection. For example, in keto isocytosine, these methods identified ring deformation as a key structural feature.³²

In addition to such structure-based classification approaches, supervised machine learning models are also being developed to predict properties related to reaction mechanisms from data obtained via molecular dynamics (MD) simulations. For example, Zakharova *et al.* employed hybrid quantum mechanics/molecular mechanics (QM/MM)-based MD trajectories

to train machine learning models capable of predicting dipole moment variations in enhanced yellow fluorescent protein chromophores.³³ Similarly, Song *et al.* used ReaxFF-based MD simulations to develop regression models for analyzing the mechanical responses of zeolites.³⁴ These studies underscore the potential of integrating MD simulations with machine learning techniques to extract chemically meaningful patterns and enhance mechanistic understanding of complex reactions.

In this study, we perform reaction path explorations and *ab initio* MD (AIMD) simulations on the full-dimensional excited-state PES to elucidate the reaction behavior of 1122C, including structural changes and their associated time scales during *trans-cis* photoisomerization. Additionally, we simulate the SE spectrum based on excited-state AIMD trajectories and examine key structural parameters beyond the torsional angle of the methine chain. To identify structural features influencing spectral changes, we applied eXtreme Gradient Boosting (XGB)³⁵ and Random Forest (RF),³⁶ both supervised machine learning algorithms, to the dataset of molecular geometries generated from the excited-state dynamics.

2. Computational details

2.1 Search for stable conformers in the electronic ground state.

The thermodynamically stable conformers of 1122C in the electronic ground state were searched using the single-component artificial force induced reaction (SC-AFIR) method,³⁷ as implemented in the GRRM17 program.^{37–39} All identified conformers were subsequently optimized and confirmed as minimum energy (MIN) structures through vibrational frequency analysis. Transition state (TS) structures between MIN structures and the corresponding intrinsic reaction coordinates (IRCs) were also computed as needed. Electronic structure calculations were performed at the ω B97XD/6-31G(d) level of density functional theory (DFT) using the Gaussian16 program.⁴⁰ It should be noted that 1122C is typically paired with an iodine counterion in the crystalline phase;⁴¹ however, in this study, the counteranion was excluded, and calculations were conducted on the closed-shell singlet (S_0) state of the 1122C cation in vacuum. Further computational details are provided in Supporting Information Section S1.

2.2 Reaction path search in the electronic excited state.

The steepest descent paths were computed from the Franck-Condon (FC) structures of the S_0 -MIN structures in the optically brightest electronic excited state. A steepest descent path initiated from a non-transition state structure is referred to as a meta-IRC.⁴² Possible MIN structures in the excited state were also searched *via* geometry optimization. Reaction paths connecting the obtained MIN structures were computed using the double-sphere artificial force induced reaction (DS-AFIR) method,^{37,38} as implemented in the GRRM17 program. Excited-state calculations were carried out using time-dependent density functional theory (TDDFT) with the ω B97XD functional and the 6-31G(d) basis set, as implemented in the Gaussian16 program.⁴⁰

Additionally, the conical intersection (CI) structure between the first excited (S_1) and ground (S_0) states was located using the branching plane updating method⁴³ in the GRRM17 program. The CI structure was optimized using the mixed-reference spin-flip (MRSF-) TDDFT approach⁴⁴ at the BHHLYP/6-31G(d) level, as implemented in the GAMESS program.⁴⁵

2.3 Excited-state *ab initio* molecular dynamics (AIMD) simulations.

To investigate the excited-state dynamics associated with *trans-cis* photoisomerization of 1122C, AIMD simulations were performed starting from the FC geometry of the S_0 -MIN structure. Initial coordinates and momenta were generated by sampling vibrational energies from a Boltzmann distribution at 300 K and assigning them to phase space variables (positions and momenta) based on the harmonic approximation of the S_0 -MIN structure. An anharmonic correction was subsequently applied to the momenta to account for deviations between the harmonic potential and the actual potential energy at the sampled coordinates. Atomic coordinates and velocities were propagated using the velocity-Verlet algorithm⁴⁶ with a time step of 1.0 fs. Convergence of the total energy with this time step was confirmed prior to the production runs. In total, fifty independent initial conditions were adopted. All AIMD simulations were performed using the SPPR program.⁴⁷ The detailed protocols of the AIMD simulations and the initial samplings are summarized in Supporting Information (see Section S3).

3. Results and Discussion

3.1 Reaction path analysis in the excited state.

Ground-state structural exploration identified three *trans* conformers and six *cis* conformers of 1122C (Figure S1). As shown in **Figure 2**, the dihedral angles at the central part of the molecule are key to distinguishing these conformers. All of the *trans* conformers were lower in energy than any of the *cis* conformers, and an energy barrier greater than 0.4 eV was found between the *trans* and *cis* conformers in the ground state. See Section S1 for details. In this study, we regarded the lowest-energy *trans* conformer (*trans1*) as the representative initial structure for photoexcitation. In the excited-state reaction path analysis, we also considered a *cis* conformer (*cis2*), which is connected to *trans1* via the IRC on the S_0 surface. Hereafter, *trans1* and *cis2* are referred to as S_0 -MIN(*trans*) and S_0 -MIN(*cis*), respectively.

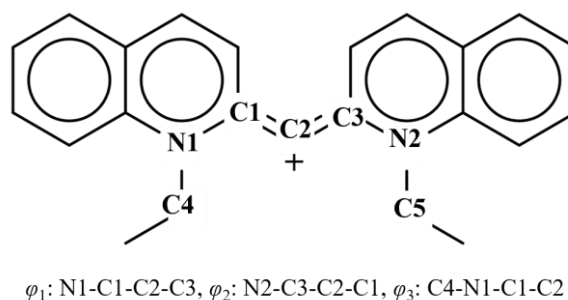


Figure 2. Atom labeling scheme for the 1122C molecule.

Based on the calculated oscillator strengths of $S_n \leftarrow S_0$ transitions at both S_0 -MIN(*trans*) and S_0 -MIN(*cis*), we confirmed that the lowest excited state (S_1) was the brightest, and that the $S_1 \leftarrow S_0$ transition corresponded to a $\pi\pi^*$ excitation (see Section S2 for details). **Figure 3(a)** shows the S_1 potential energy profile along the meta-IRC from the FC geometries, plotted as a function of the torsional angle $\varphi(\text{N1-C1-C2-C3})$. From S_1 -FC(*trans*), which represents the S_1 Franck-Condon geometry of S_0 -MIN(*trans*), the meta-IRC (path1) leads to the minimum

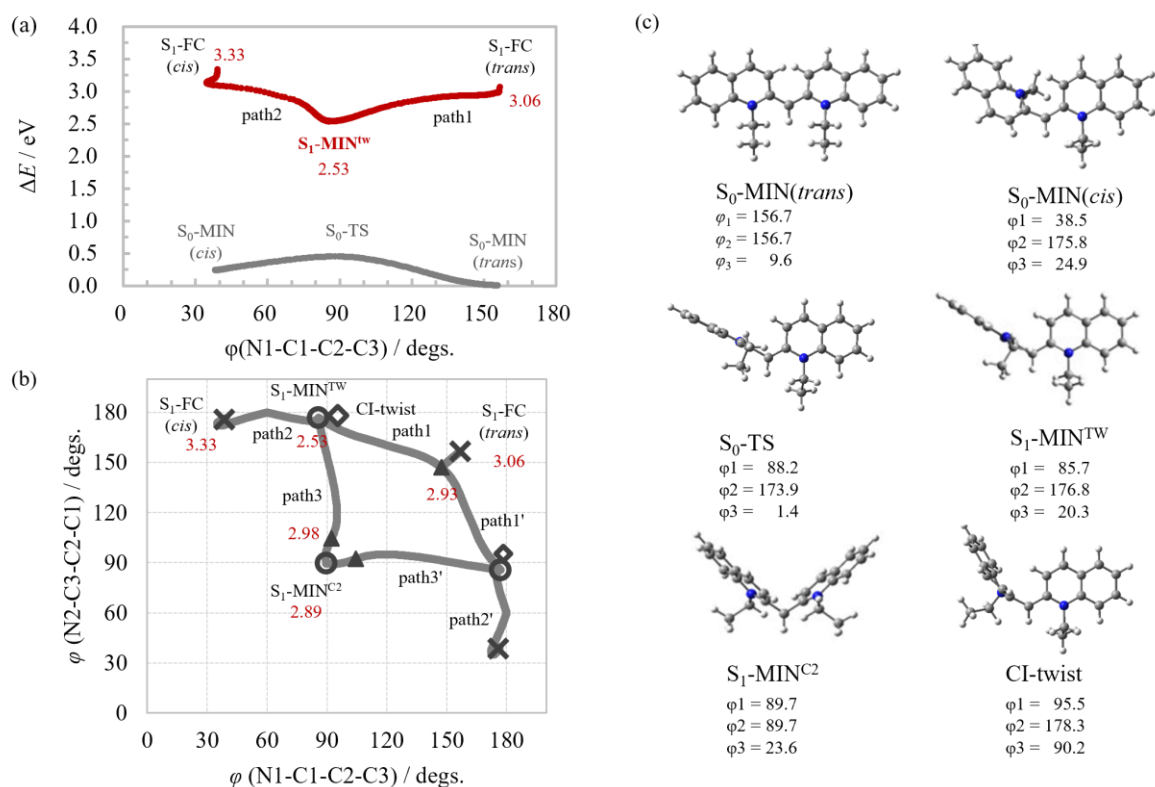


Figure 3. (a) Potential energy profile along the twisting coordinate ($\phi(\text{N1-C1-C2-C3})$) of the quinoline ring, obtained from the meta-IRC path originating from the FC structure in the *trans* and *cis* region. Energies are given relative to the lowest-energy ground-state structure, S_0 -MIN(*trans*). (b) Significant points and reaction pathways on the S_1 -PES projected onto two-dimensional coordinate space by the twisting angles $\phi(\text{N1-C1-C2-C3})$ and $\phi(\text{N2-C3-C2-C1})$ of both quinoline rings. Minimum energy (MIN), transition state (TS), and conical intersection (CI) structures are indicated by open circles ($\circ$), triangles ($\blacktriangle$), and open squares ($\square$), respectively. Path1 and path2 correspond to the meta-IRCs starting from S_1 -FC(*trans*) and S_1 -FC(*cis*), respectively, which denote the Franck-Condon states of S_0 -MIN(*trans*) and of S_0 -MIN(*cis*), respectively. Path3 corresponds to the IRC connecting S_1 -MIN^{tw} and S_1 -MIN^{C2}. (c) Representative molecular structures from panels (a) and (b), with key internal coordinates shown below each structure.

energy structure $S_1\text{-MIN}^{\text{TW}}$. In this structure, one of the quinoline rings is twisted by 85.71° relative to the plane of the other. It is noteworthy that the meta-IRC (path2) from $S_1\text{-FC}(\text{cis})$ also reaches the same $S_1\text{-MIN}^{\text{TW}}$ structure. We observed that the S_1 PES exhibits no barrier between the $S_1\text{-FC}$ structures and $S_1\text{-MIN}^{\text{TW}}$, with an energy difference of approximately 1 eV. This flat potential energy profile is consistent with the barrierless behavior inferred from transient absorption spectroscopy experiments.²⁶ As shown in Figure 3, $\Delta E(S_1-S_0)$ decreases upon twisting. This behavior can be attributed to the asymmetric response of S_0 and S_1 to such rotational structural changes. Specifically, twisting reduces the overlap of p orbitals, destabilizing the π bond and increasing the energy of S_0 , while S_1 is less affected. Consequently, the energy gap $\Delta E(S_1-S_0)$ decreases.

To further clarify the topology of the S_1 -PES, we analyzed reaction pathways associated with *trans-cis* photoisomerization, focusing on the twist motions of both quinoline rings. Figure 3(b) represents the reaction pathways projected onto a two-dimensional coordinate space in terms of the twist angles $\varphi(\text{N1-C1-C2-C3})$ and $\varphi(\text{N2-C3-C2-C1})$. This figure includes: (i) the meta-IRC (path1) originating from $S_1\text{-FC}(\text{trans})$, (ii) the meta-IRC (path2) from $S_1\text{-FC}(\text{cis})$, and (iii) the IRC (path3) connecting $S_1\text{-MIN}^{\text{TW}}$ and $S_1\text{-MIN}^{\text{C2}}$, the latter being a structure with C_2 symmetry. The meta-IRC (path1) originating from $S_1\text{-FC}(\text{trans})$ initially preserves C_2 symmetry and passes through a TS with the same symmetry. The imaginary vibrational mode at this TS breaks the C_2 symmetry, reducing it to C_1 , and the subsequent IRC leads to the $S_1\text{-MIN}^{\text{TW}}$ structure. Notably, the diagonal line in Figure 3(b) corresponds to structures retaining C_2 symmetry. Path pairs, 1/1', 2/2', and 3/3', are energetically equivalent and differ only in the direction of internal torsional motion. Starting from the $S_1\text{-MIN}^{\text{TW}}$ structure, CI optimization at the MRSF-TDDFT level identified a minimum energy CI (MECI) structure (Figure 3(c)), with a relative energy of 0.61 eV compared to the $S_1\text{-MIN}^{\text{TW}}$ structure at this computational level. This MECI structure exhibits a twisted ring geometry similar to that of $S_1\text{-MIN}^{\text{TW}}$, with

one of the quinoline rings rotated by approximately 90° ; however, it features a pyramidalized nitrogen atom in the twisted ring. These results suggest that, in the early stage of excited-state dynamics, the twisting motion of one quinoline ring is enhanced, and non-radiative decay from the CI-twist region may occur on a longer time scale.

3.2 Stimulated emission simulation via excited-state AIMD calculations.

SE spectra were simulated based on AIMD trajectories initiated from the FC structure in the *trans* region. Figure 4(a) presents the theoretical SE spectra as a function of simulation time, constructed by counting the number of trajectories contributing to each wavelength range (S_1 - S_0 energy difference in nm) at each time step. The data were generated under the assumption that, at any given time, all molecules present in each spatial region undergo emission ("dumping"). The results show a rapid decrease in the short-wavelength component (350–550 nm; violet and blue) within the first 300 fs, accompanied by a corresponding increase in the 550–750 nm range (cyan and emerald green). This behavior indicates that the trajectory ensemble departs from the FC region and relaxes toward the S_1 -MIN^{TW} region. Subsequently, the 750–850 nm component (green) increases gradually from 300 fs to 500 fs, followed by a slight increase in the 850–950 nm component (yellow). These changes suggest that the system remains in a quasi-stable state after reaching the S_1 -MIN^{TW} region. These SE redshift behaviors were quantitatively reproduced by the time evolution of the SE spectrum in Figure 4(c). Figure 4(b) compares the rise time constants obtained from theoretical fitting of the spectral evolution (Figure 4(a)) using an exponential function, with those measured in a previous transient absorption experiment.²⁶ The agreement between theoretical and experimental time constants supports the reliability of the simulated SE spectra and confirms that the AIMD-based dynamics capture the essential features of the observed photophysical behavior.

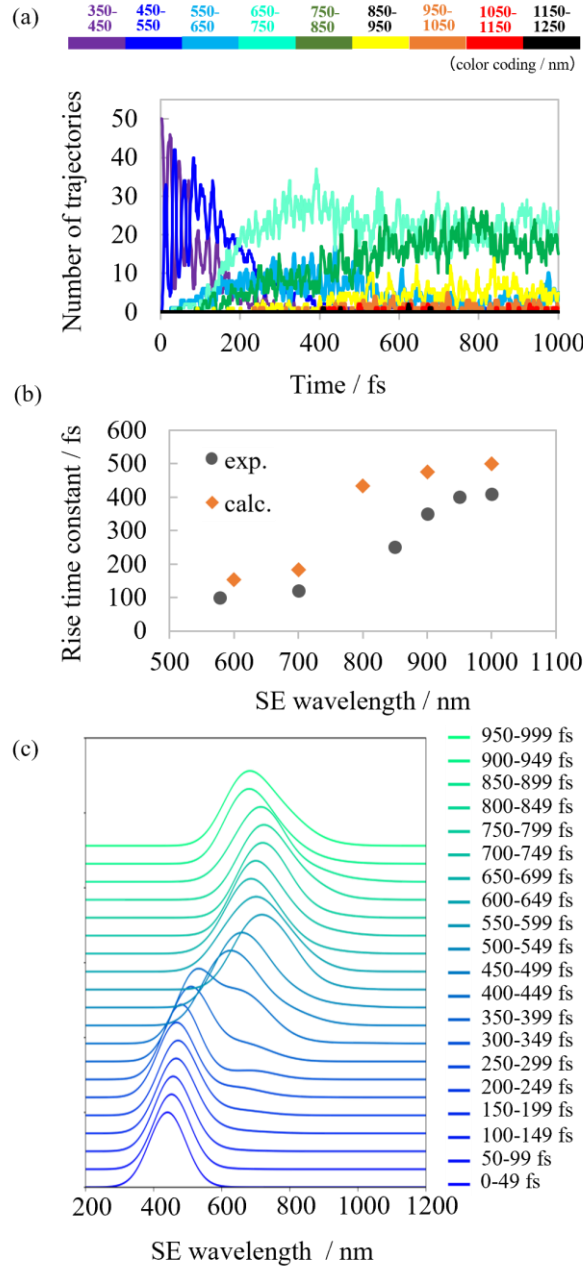


Figure 4. (a) Theoretical SE spectra based on AIMD trajectories. The line color represents the S_1 - S_0 energy difference corresponding to the SE wavelength, categorized as follows: violet (350–450 nm), blue (450–550 nm), cyan (550–650 nm), emerald green (650–750 nm), green (750–850 nm), yellow (850–950 nm), orange (950–1050 nm), red (1050–1150 nm), and black (1150– nm). (b) Comparison of the rise time constants for the SE signal obtained from theory and experiment.²⁶ Black circles and orange diamonds indicate experimental and theoretical results, respectively. (c) Time evolution of the SE spectrum, shown in 50 fs intervals.

To interpret the theoretical SE spectrum in terms of the movement of the trajectory ensemble, we projected the AIMD trajectories onto the two-dimensional coordinate space defined by the twisting angles of the left and right quinoline rings. Figure 5(a) shows the distribution of 50 trajectories on this coordinate space, with marker color indicating the S_1-S_0 energy difference corresponding to the SE wavelength. Although the trajectories appear to bifurcate into two branches, this merely reflects differences in which quinoline ring is initially twisted, due to random sampling during initial condition generation. At $t = 0$ fs, the trajectories are distributed around the S_1 -FC structure in the *trans* region, producing SE wavelengths in the 350–450 nm range. As the dynamics proceed, the trajectory ensemble relaxes along the slope of the S_1 -PES toward the S_1 -MIN^{TW} region, resulting in a redshift of the SE wavelength to approximately 700 nm within the first 300 fs. This behavior is consistent with the excited-state PES profile shown in Figure 3(a) and the temporal evolution of the theoretical SE spectrum in Figure 4(a). Between 300 fs and 500 fs, nearly all trajectories remain localized near the S_1 -MIN^{TW} structure. After 500 fs, the ensemble continues to reside in the vicinity of the twisted region. These dynamics correlate with the dominance of the 650–850 nm SE components (emerald green and green) in the simulated spectrum. Importantly, none of the trajectories reach the S_1 -MIN^{C2} regions within the 1000 fs simulation window, suggesting that once the system enters either of the two wells of S_1 -MIN^{TW}, the internal energy becomes concentrated in the twisting motion of one of the quinoline rings, making it difficult to escape from that state.

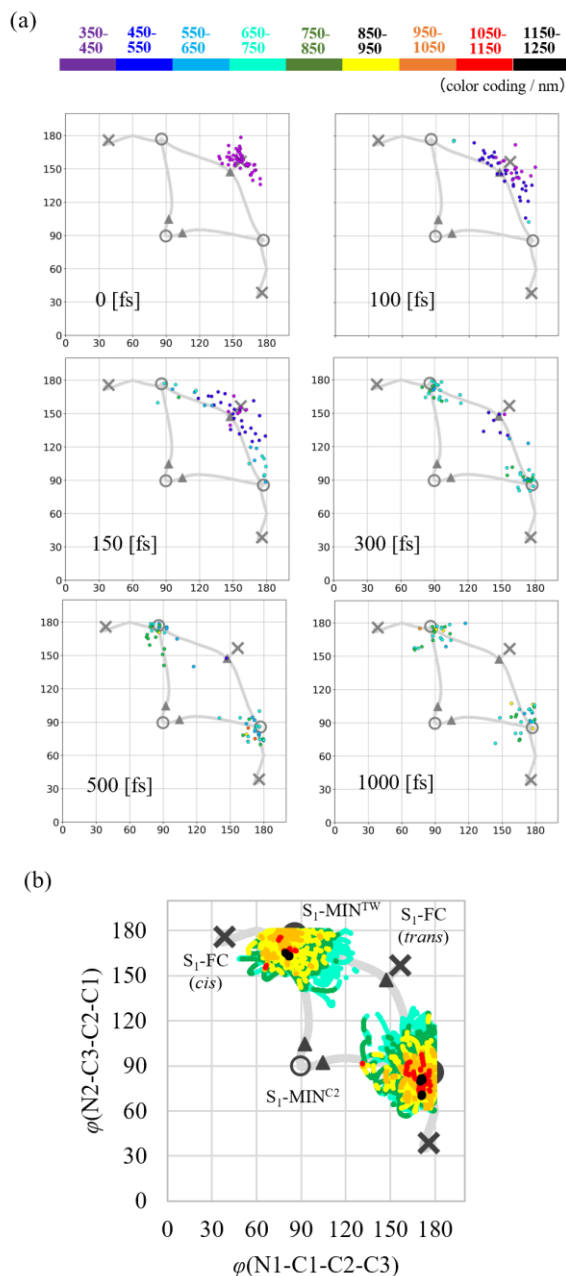


Figure 5. (a) Projection of 50 AIMD trajectories onto a two-dimensional space defined by the twisting angles of the left and right quinoline rings. Snapshots are shown at $t = 0, 100, 150, 300, 500,$ and 1000 fs. (b) Trajectory snapshots corresponding to stimulated emission wavelengths longer than 650 nm. Marker color represents the S_1-S_0 energy difference, corresponding to the stimulated emission wavelength, as follows: violet (350–450 nm), blue (450–550 nm), cyan (550–650 nm), emerald green (650–750 nm), green (750–850 nm), yellow (850–950 nm), orange (950–1050 nm), red (1050–1150 nm), and black (> 1150 nm).

Previous studies have interpreted that the longest SE wavelength is achieved when the nuclear wave packet reaches the bottom of the excited state PES. Based on this interpretation and the results of reaction path calculations, the maximum SE wavelength should correspond to the S_1 - S_0 energy gap at the S_1 -MIN^{TW} structure, which is calculated to be 707 nm. However, Figure 5(b) presents snapshots of trajectories exhibiting SE wavelengths in the 650–750 nm range or longer, revealing that many trajectories exceed this expected limit. Notably, the longest SE wavelength observed in our simulations reaches 1185 nm. Furthermore, projection of these long-wavelength trajectories onto the two-dimensional space defined by the twist angles of both quinoline rings shows that SE components in the yellow, orange, red, and black ranges are not confined to the vicinity of the S_1 -MIN^{TW} structure but are also distributed in regions farther from it. These findings are inconsistent with the one-dimensional potential energy profile along the twist coordinate shown in Figure 3(a), and contradict the prevailing intuitive interpretation that associates the longest SE wavelength with the global minimum of the excited-state PES. This apparent discrepancy prompted us to investigate structural features beyond the twist angles of the quinoline rings to better understand the origin of the enhanced SE wavelengths observed in the trajectory ensemble evolving on the flat S_1 -PES.

3.3 Examination of internal coordinates contributing to excited-state dynamics.

To identify key structural coordinates responsible for the increase in SE wavelength beyond 650 nm, we performed a structure-property relationship analysis using the eXtreme Gradient Boosting (XGB)³⁵ and the Random Forest (RF),³⁶ supervised machine learning methods. Both methods enable the evaluation of feature importance in regression tasks, thereby elucidating the relationship between molecular geometry and SE wavelength. In this study, we constructed regression models using these methods to predict SE wavelength from a set of 264 redundant geometric features derived from 16,492 molecular structures exhibiting $\Delta E(S_1-S_0)$

corresponding to SE wavelengths of 650 nm or greater, sampled from all AIMD trajectory snapshots. The resulting models achieved coefficients of determination (R^2) of 0.95 for XGB and 0.78 for RF on the validation data, indicating substantially higher predictive accuracy for XGB. Therefore, in the subsequent structural–property relationship analysis, we focused on the results obtained with the XGB model rather than the RF model. These methods were performed using the implementation available in the Scipy library within the Python environment. Further details on model construction and feature processing are provided in Supporting Information Section S4.

Figure 6(a) presents the five most important internal coordinates contributing to the long-wavelength components of the SE signal, as identified by the XGB model. Among the identified features, $\phi(\text{C4-N1-C2-C3})$, representing “ring distortion”, is the most influential, followed by $r(\text{C2-C3})$, corresponding to the “C=C stretch”. The importance values for all remaining coordinates are minimal and nearly equivalent. Notably, the dominant “ring distortion” coordinate corresponds to the internal structural deformation observed in the CI-twist structure shown in Figure 3(c). This finding indicates that the enhanced SE wavelengths observed on the relatively flat S_1 -PES arise from structural distortions that significantly raise the S_0 energy while leaving the S_1 energy largely unchanged. Another important features - stretching of the methine (C=C) bridge was objectively identified by the machine learning model without reliance on prior assumptions.²³ It is worth noting that the significance of coordinates such as ring distortion has been highlighted in studies applying unsupervised learning to analyze CI geometries.^{31,32}

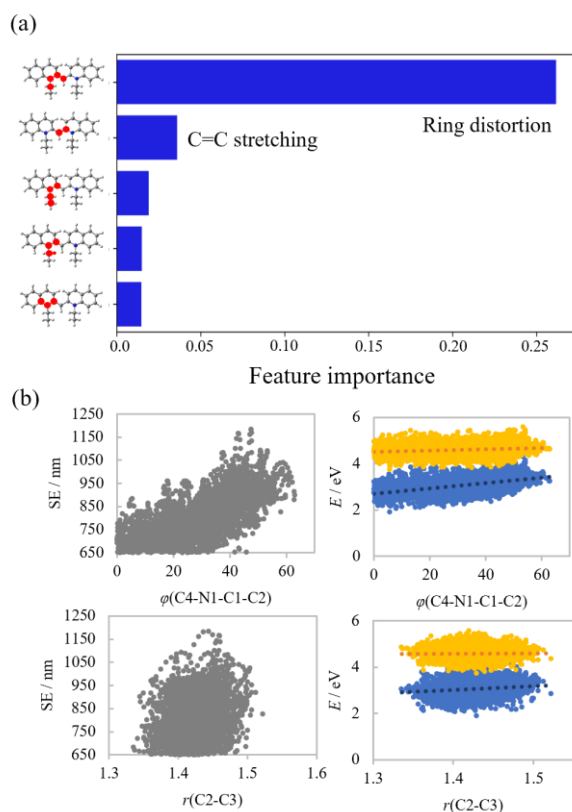


Figure 6. (a) Top five internal coordinates with the highest feature importance identified by the XGB analysis. (b) SE wavelength, S_0 potential energy, and S_1 potential energy plotted as functions of the top two internal coordinates shown in (a).

To gain deeper insight into the roles of these three internal coordinates, we analyzed their relationships with the SE wavelength. Figure 6(b) presents the SE wavelength, S_0 energy, and S_1 energy as functions of the two most important internal coordinates - "ring distortion" and "C=C stretch" – based on trajectory snapshots with SE wavelengths longer than 650 nm. Focusing on the dominant "ring distortion" coordinate, we observe a clear increase in S_0 energy as the distortion becomes more pronounced. Similar trends are found for the "C=C stretch" coordinates, which are positively correlated with increases in S_0 energy. The correlation plots presented in Figure S6 further support these findings, demonstrating that a redshift in SE wavelength occurs when two coordinates increase simultaneously. These results lead to the

conclusion that SE wavelengths exceeding 650 nm are primarily enhanced by "ring distortion" – characterized by the pyramidalization of the nitrogen atom - as well as by structural changes involving C=C bond stretching. In combination with the quinoline ring twist, these deformations drive the system to regions of the excited-state PES where the S_0 – S_1 energy gap is reduced, resulting in longer-wavelength SE emission.

4. Concluding Remarks

Through theoretical spectroscopy, we revisited the interpretation of experimentally observed SE spectra of 1122C in the excited state. Experimental studies have attributed the redshift of the SE wavelength to the descent of the nuclear wave packet along the S_1 -PES, primarily driven by the twisting motion of the quinoline ring. These studies assumed that the longest SE wavelength occurred at the bottom of the excited-state PES. Our theoretical SE spectra, derived from AIMD trajectories, support the time-dependent redshift of the SE signal associated with quinoline ring twisting, confirming that the S_1 -PES is essentially flat and barrierless along this coordinate. This validates the twisting motion as a principal reaction coordinate for the photoisomerization of 1122C. However, our simulations revealed that the longest SE wavelengths do not originate precisely from the S_1 -MIN^{Tw} structure but rather from surrounding regions, suggesting the involvement of additional internal coordinates. To identify these, we applied the XGB and RF machine learning algorithms and uncovered three key structural features contributing to SE redshift: ring distortion and C=C bond stretching. These deformations were found to significantly elevate the S_0 energy while leaving the S_1 energy largely unaffected - characteristics also observed in the CI structure. Thus, our combined approach of theoretical spectroscopy and machine learning demonstrates that redshift in SE wavelengths is enhanced when these structural changes occur in concert with the twisting of the quinoline ring. This suggests that while quinoline ring twisting is the primary factor influencing the SE spectrum in the early stages of the simulation, the redshift observed in the later stages is predominantly driven by these internal coordinate deformations.

For future work and closer integration with experimental studies, we plan to extend our methodology to simulate theoretical SE spectra for solution-phase reactions by incorporating solvent effects into excited-state AIMD simulations.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.

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