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UNIVERSITY OF CALIFORNIA,
IRVINE

From electronic structure to spectra: advancing quantum chemical methods for
excited-state processes

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Sourav Majumdar

Dissertation Committee:
Professor Filipp Furche, Chair
Professor Craig Martens
Professor Ioan Andricioaei

2025

DEDICATION

Dedicated to my parents,
who always believed in me and gave me wings to pursue my dreams.

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1. S. Majumdar, R. Grotjahn, A. Rajabi, B. Feng, L. N. Mohanam, G. S. Phun, N. Lutfi, M. Khan, D. Rappoport, and F. Furche. Mechanism of the non-Kasha fluorescence in pyrene. *J. Comput. Chem.*, 46(3):e70040, **2025**.
2. J. Franzke, C. Holzer, J. H. Andersen, T. Begušić, F. Bruder, S. Coriani, F. Della Sala, E. Fabiano, D. A. Fedotov, S. Fürst, S. Gillhuber, R. Grotjahn, M. Kaupp, M. Kehry, M. Krstić, F. Mack, S. Majumdar, B. D. Nguyen, S. M. Parker, F. Pauly, A. Pausch, E. Perlt, G. S. Phun, A. Rajabi, D. Rappoport, B. Samal, T. Schrader, M. Sharma, E. Tapavicza, R. S. Treß, V. Voora, A. Wodyński, J. M. Yu, B. Zerulla, F. Furche, C. Hättig, M. Sierka, D. P. Tew, and F. Weigend. TURBOMOLE: Today and tomorrow. *J. Chem. Theory Comput.*, 19(20):6859–6890, **2023**.
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Mechanism of the non-Kasha fluorescence in pyrene
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ABSTRACT OF THE DISSERTATION

From electronic structure to spectra: advancing quantum chemical methods for
excited-state processes

By

Sourav Majumdar

Doctor of Philosophy in Chemistry

University of California, Irvine, 2025

Professor Filipp Furche, Chair

Photochemical processes play a central role in chemistry and biology, governing phenomena such as fluorescence, chemiexcitation, and bioluminescence. Despite their importance, accurately simulating these processes remains a major challenge due to the need to describe coupled electronic and nuclear dynamics over multiple timescales.

The development, implementation, and benchmarking of computational methods for studying photochemical processes and computing associated spectroscopic observables are reported in this dissertation. Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were used for the underlying electronic structure calculations. Vibronic perturbation theory (VPT) and fewest switches surface hopping (FSSH) were applied to simulate and explain the gas-phase fluorescence of pyrene. Together, VPT and FSSH were established as a two-step approach for investigating nonadiabatic effects in the absorption and emission spectra of molecular systems.

A methodology was established to compute time-resolved spectroscopic observables, such as the transient absorption (TA) spectrum, from multi-state FSSH simulations. The computed TA spectrum of pyrene was found to agree with experiment.

DFT and TDDFT were further employed to simulate the absorption spectra of novel 2.2.2-cryptand complexes of neptunium(III) and plutonium(III), and to determine the minimum-energy conformers of nicotinamide cofactor biomimetics. The results are consistent with experimental observations.

Finally, an integrated framework combining weighted-ensemble ab initio molecular dynamics with nonadiabatic molecular dynamics was developed to study the bioluminescence of dinoflagellate luciferin. The computed bioluminescence spectra and mechanistic details show agreement with experiment and previous studies. This framework provides a generalizable strategy for simulating long-timescale processes and excited-state dynamics in complex photochemical systems.

Chapter 1

Introduction to the thesis

1.1 Advancing quantum chemical methods for excited-state processes

The accurate description of excited-state processes remains one of the central challenges in quantum chemistry. Photophysical and photochemical phenomena such as fluorescence, chemiexcitation, and bioluminescence involve complex couplings between electronic and nuclear degrees of freedom, requiring theoretical methods that can bridge electronic structure with spectroscopy.

Over the past decades, a variety of electronic structure methods have been developed to treat excited states. Wavefunction-based approaches such as configuration interaction singles (CIS), algebraic diagrammatic construction (ADC) [3], and coupled-cluster response theory (e.g., CC2, CCSD)[4] provide a systematically improvable description of electronic excitations but remain computationally demanding, limiting their routine application to small and medium-sized molecules. Density functional theory (DFT) and, in particular,

time-dependent density functional theory (TDDFT) have emerged as widely used alternatives due to their favorable balance of accuracy and efficiency [5–7].

On the dynamics side, surface-hopping of different flavors [8–12] is one of the most common common semiclassical approaches for simulating coupled electronic-nuclear motion in the excited state. While successful in capturing many nonadiabatic processes, they often require large numbers of trajectories to achieve statistical convergence and may fail in regimes with strong decoherence. Similarly, vibronic structure in spectroscopy is typically described by Franck–Condon and Herzberg–Teller approximations, but these approaches neglect nonadiabatic couplings that become critical for complex emission processes [13, 14].

This dissertation, titled *From electronic structure to spectra: advancing quantum chemical methods for excited-state processes*, presents the development and application of computational approaches that extend the applicability of DFT and TDDFT. Vibronic perturbation theory (VPT) and nonadiabatic molecular dynamics (NAMD) are combined to simulate steady-state fluorescence and to investigate deviations from Kasha’s rule in prototypical systems such as pyrene. A framework for extracting time-resolved observables, including transient absorption spectra, is established from multi-state NAMD simulations, enabling direct comparison with ultrafast experiments.

Beyond small organic chromophores, the methods are applied to more complex systems. Weighted-ensemble *ab initio* molecular dynamics combined with NAMD provides a generalizable strategy for simulating long-timescale processes, demonstrated here in the context of dinoflagellate luciferin bioluminescence. In addition, electronic structure studies of nicotinamide DNA cofactors and actinide cryptand complexes illustrate how carefully benchmarked DFT/TDDFT protocols can reproduce oxidation potentials and absorption spectra, thereby guiding experimental interpretation.

Overall, this work advances the connection between quantum chemistry and spectroscopy,

demonstrating how electronic structure theory can be systematically extended to describe excited-state dynamics and to predict spectroscopic observables.

Chapter 2

Mechanism of the non-Kasha fluorescence in pyrene

This chapter contains verbatim excerpts from “ S. Majumdar, R. Grotjahn, A. Rajabi, B. Feng, L. N. Mohanam, G. S. Phun, N. Lutfi, M. Khan, D. Rappoport, and F. Furche. Mechanism of the non-Kasha fluorescence in pyrene. *J. Comput. Chem.*, 46(3):e70040, 2025.”

Author contribution of Sourav Majumdar : Conceptualization (equal), Methodology (lead), Software (lead), Validation (lead), Formal analysis (lead), Investigation (lead), Data Curation (equal)

2.1 Introduction

The steady-state fluorescence of many stable (singlet) organic molecules is adequately described by the empirical Kasha’s rule, which posits that their emission should only proceed

from their S_1 states.[15] The conventional rationale for Kasha’s rule is that the internal conversion (IC) from $S_n \rightarrow S_1$ ($n > 1$) is typically very fast compared to the S_1 fluorescence lifetime. Steady-state non-Kasha fluorescence can arise through several distinct mechanisms [16–21], posing a difficult challenge for electronic structure and quantum dynamics methods; it has important applications, e. g., the design of dually fluorescent dyes for biological imaging or artificial photosynthesis.[17, 19, 22] Pyrene and some of its derivatives, such as benzopyrene, obey Kasha’s rule in solution [23], the gas-phase fluorescence is more complex, with an additional high-energy emission ($> 3.4\text{ eV}$) [1, 17, 20, 24, 25]. The high-energy shoulder is enhanced in a collision-free environment and is diminished when the pressure of the inert gas in the reaction mixture is increased.[25–27]

Here we consider the non-Kasha fluorescence of pyrene in the gas phase within equilibrium response theory and semiclassical nonadiabatic molecular dynamics (NAMD). Equilibrium response theory, specifically vibronic perturbation theory, provided the first successful rationale for pyrene’s non-Kasha emission in the 1970s [13, 28–30]. It is suitable for steady-state processes and longer timescales, and inexpensive enough to allow for quantum nuclear treatment, typically within the rigid rotor-harmonic oscillator (RRHO) model. However, this approach requires *a priori* knowledge of the critical points (equilibrium structures, conical intersections) of the relevant potential energy surfaces (PESs). Moreover, electronic structure methods capable of providing potential energy surface and derivative couplings accurate enough to test vibronic perturbation theory for molecules of the size of pyrene have become available only in the recent past.

Semiclassical NAMD simulations [6, 8] using high-level electronic structure methods to compute energies, gradients, and nonadiabatic couplings on-the-fly were pioneered by Lischka and co-workers [31, 32] and have been increasingly used to study ultrafast processes far from equilibrium. While NAMD simulations require little prior knowledge and can be considered “computational experiments”, longer timescales in the ps to ns regime are computationally

demanding for larger polyatomic molecules. Recently, Isborn and co-workers [33] have shown that NAMD simulations may fail to reproduce vibronic effects which can be attributed to the fact that the nuclei are treated semiclassically.[33] Vibronic effects in the emission spectrum of pyrene have been studied extensively [14, 34–38] and thus offer a good test case for a comparative assessment of equilibrium response theory vs. NAMD simulations.

A recent study by Barbatti and co-workers [21] used NAMD simulations with the second-order Algebraic Diagrammatic Construction (ADC(2)) [3, 39] to study the non-Kasha fluorescence of pyrene in the gas phase. The couplings between the electronic states were calculated using the local diabaticization algorithm [40] and the spectrum was calculated by averaging over a large number of time steps. The non-Kasha fluorescence was found to result from a dynamic equilibrium between the S_1 and S_2 states, leading to a significant contribution from the bright S_2 state in the emission spectrum. The strong nonadiabatic coupling between the S_1 and S_2 states suggests the presence of an accessible conical intersection (CI) between S_1 and S_2 adiabatic PESs. Maeda and co-workers [41] investigated CIs between the ground (S_0) and the S_1 states of pyrene and similar polycyclic aromatic hydrocarbons and found a correlation between the energy barrier to the CI and the fluorescence quantum yield. Robb and co-workers [42] explored the CI between the first two excited states of the pyrene radical cation to understand its role in the diffuse interstellar bands. The existence of such a CI and its role in the S_2 to S_1 ultrafast relaxation was studied by de Vivie-Riedle and co-authors [43] using both semiclassical and quantum dynamics simulations.

A key question addressed in this work is whether the non-Kasha fluorescence of pyrene can be understood in terms of static vibronic mixing or whether it is a fundamentally dynamic effect resulting from an equilibrium between the S_1 and S_2 states. We simulate the emission spectrum of pyrene by vibronic perturbation theory using parameters obtained from time-dependent density functional theory (TDDFT) calculations. We also perform fewest-switches surface hopping (FSSH) NAMD simulations [8] at the same level of elec-

tronic structure theory.[6, 7, 44–46] In Section 2.2, we describe the theoretical methods used in this study. In Section 2.3, we present the results of our vibronic perturbation theory and NAMD simulations. These two approaches are compared in Section 2.4, and we present conclusions in Section 2.5.

2.2 Methods

2.2.1 Vibronic Perturbation Theory

Conventional vibronic perturbation theory uses fixed-position (crude adiabatic) Born-Oppenheimer [47–49] (BO) wavefunctions as the basis for the perturbation expansion and treats the dependence of the electronic wavefunction on the nuclear coordinates as a perturbation.[29, 30] The zero-order terms in the perturbation expansion are the Franck–Condon (FC) contributions, while the first-order terms are the Herzberg–Teller (HT) terms. In this paper, we start from adiabatic BO electronic states within the RRHO (rigid rotor harmonic oscillator) approximation as our zero-order states in the spirit of Ref. [50]. The BO RRHO spectra including FC factors and Dushinsky rotation are efficiently computed using the generating function approach [2, 51]. We then consider HT coupling and first-order nonadiabatic couplings (FONAC), $\mathbf{F}_{nm} = \langle \Phi_n | \frac{\partial}{\partial R} \Phi_m \rangle$ with respect to nuclear coordinates R between adiabatic states Φ_n and Φ_m as a perturbation. Within the dipole approximation, the isotropically averaged first-order photon emission rate from a fixed initial state i is given by [50]

$$\sigma_{\text{em}}(\omega) = \frac{4\omega^3}{3c^3} \sum_f |\boldsymbol{\mu}_{if}|^2 G(\omega - \omega_{if}). \quad (2.1)$$

The transition dipole moment

$$\boldsymbol{\mu}_{if} = \langle \Psi_i | \hat{\boldsymbol{\mu}} | \Psi_f \rangle \quad (2.2)$$

is defined in terms of eigenstates of the full molecular Hamiltonian, Ψ_i and Ψ_f , whose energy difference is ω_{if} . ω denotes the emission energy, $G(\omega)$ is a normalized lineshape function, and c denotes the speed of light. Atomic (Hartree) units are used throughout; in these units, energies and (angular) frequencies are identical, since $\hbar = 1$. Eq. (2.1) can be extended to finite temperature by considering an ensemble initial state [50].

We expand the transition dipole moment $\boldsymbol{\mu}_{if}$ around its BO-RRHO value $\boldsymbol{\mu}_{if}^{(0,0)}$ as

$$\boldsymbol{\mu}_{if} = \boldsymbol{\mu}_{if}^{(0,0)} + \boldsymbol{\mu}_{if}^{(0,1)} + \boldsymbol{\mu}_{if}^{(1,0)} + \boldsymbol{\mu}_{if}^{(1,1)} + \text{higher-order terms.} \quad (2.3)$$

$\boldsymbol{\mu}_{if}^{(0,1)}$ accounts for the first-order HT correction to $\boldsymbol{\mu}_{if}^{(0,0)}$, whereas $\boldsymbol{\mu}_{if}^{(1,0)}$ corrects for FONAC; $\boldsymbol{\mu}_{if}^{(1,1)}$ is a second-order correction taking both effects into account. Computing the HT corrections using finite differences for the S_1 state of pyrene is numerically nontrivial and requires careful convergence studies, see Supporting Information (SI). FONAC corrections were evaluated using analytical first-order nonadiabatic couplings [7, 52, 53]; the only intermediate state giving rise to significant nonadiabatic couplings at the S_1 minimum structure is S_2 . The thus obtained HT corrections to the transition dipole moment were found to be more than two orders of magnitude smaller in magnitude than the FONAC corrections. Moreover, $\boldsymbol{\mu}_{if}^{(1,0)}$ and $\boldsymbol{\mu}_{if}^{(0,0)}$ are orthogonal by symmetry. The lowest-order correction to the BO-RRHO emission spectrum of pyrene is thus

$$\Delta\sigma_{\text{em}}(\omega) = \frac{4\omega^3}{3c^3} \sum_f |\boldsymbol{\mu}_{if}^{(0,1)}|^2 G(\omega - \omega_{if}). \quad (2.4)$$

The lineshape was assumed to be Gaussian with an empirically chosen root mean square (RMS) width of 0.058 eV. The theoretical spectrum was red-shifted by 0.45 eV to facilitate comparison to the experimental spectrum [1].

2.2.2 NAMD Simulations

Electronic Structure Multi-state NAMD simulations [6, 7] were performed using the fewest-switches surface hopping methods using density functional theory (DFT) with the PBE0 functional [54] along with D3-dispersion corrections.[55] Excitation energies [56–59], excited-state gradients [5, 60, 61], ground-to-excited state FONAC vectors [52] were computed using the Tamm–Dancoff approximation (TDA) [59, 62, 63]. The TDA approximation to TDDFT is known to describe the L_a and L_b states of polycyclic aromatic hydrocarbons more accurately than full TDFFT and also provides reliable absorption and fluorescence spectrum band shapes [64–66]. The FONAC vectors between excited states were computed from quadratic response TDDFT in the wavefunction approximation [7, 53, 67, 68]. def2-SVPD basis sets were used for carbon [69, 70], and def2-SVP basis sets were used for hydrogen [69]. The initial conditions for the NAMD simulations were sampled from a 10 ps long ground-state molecular dynamics simulation after an equilibration period of 0.5 ps. The ground-state calculations used def2-SVP basis sets throughout. The molecular dynamics trajectories were propagated using the leapfrog Verlet algorithm [71] with the time step of 20 a. u. The same time step size was used for the propagation of NAMD trajectories. A microcanonical ensemble of trajectories was initiated from both S_1 and S_2 states to replicate the excited state dynamics of pyrene in a collision-free regime. All calculations were performed with the TURBOMOLE program suite, Version V7.5 [72, 73]. The NAMD simulations were performed using the EGRAD [60] and FROG [74, 75] modules of TURBOMOLE.

Trajectory Analysis and Spectroscopic Observables The electronic properties of a trajectory at any given time are determined by a single Born–Oppenheimer electronic state, referred to as the active state. The instantaneous population $p_m(t)$ of an electronic state S_m ($m = 0$ corresponds to the ground state) was computed from the proportion of trajectories with active state m at time t . The lifetime of the S_2 state was estimated by fitting the

decay of the state population to an exponential function. The 95% confidence intervals for the state populations were calculated using bootstrap resampling with 10 000 bootstrap samples.[7, 76, 77]

The fluorescence emission spectrum was computed by averaging the instantaneous emission spectrum over the trajectory ensemble [78] after an initial equilibration period of 0.5 ps. Instantaneous emission spectra were evaluated according to Eq. (2.1), using the excitation energies and electronic BO transition dipole moments of the active state. A Gaussian linewidth function with an empirical RMS linewidth of 0.01 eV was used. The theoretical spectrum was red-shifted by 0.45 eV to facilitate comparison to the experimental spectrum [1].

Conical Intersection and Intersection Space The minimum energy CI (MECI) between the S_1 and S_2 adiabatic states was obtained using the CI optimization algorithm of Maeda and co-workers [79] implemented in the ORCA program package [80]. The energy gap, $E_2 - E_1$, at the MECI was found to be less than 1 meV, which is on the same order of magnitude as the convergence criterion used for the excited state calculations. The intersection space vectors, the nonadiabatic coupling ($\mathbf{h}$) and the difference gradient ($\mathbf{g}$) were computed at the S_1/S_2 MECI geometry. The $\mathbf{g}$ and $\mathbf{h}$ vectors were used to generate a 12×12 2D grid of pyrene structures centered on the MECI structure by nuclear displacement in Cartesian space. At each grid point, a single-point TDDFT calculation was performed. The minimum energy structures of the S_m ($m = 0, 1, 2$) were optimized. All calculations were performed using the TDA approximation to TDDFT with the PBE0 functional, def2-SVPD basis set and D3-dispersion corrections. The projections of these critical points on the two-dimensional intersection space were located by minimizing the root mean square distances (RMSD) between optimized global minimum energy structures and the ones from the generated PES. The RMSD between two structures were computed using the quaternion

algorithm [81] using the open-source rmsd program [82].

2.3 Results

2.3.1 Excited States of Pyrene

The two lowest-lying adiabatic electronic excited states (S_1 and S_2) of pyrene are involved in the photoexcitation and photoemission process in the UV-visible region. These two adiabatic electronic states have either bright L_a or dark L_b diabatic state characters with the transition dipole moment aligned along the short and long axis of the molecule respectively according to Platt’s notation [38, 83]. We observed that the L_a state mainly results from a highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) transition while the L_b state mainly results from a near equal mixture HOMO to LUMO + 1 and HOMO-1 to LUMO transitions in agreement with previous computational studies [84]. At the ground state minimum or the FC point, S_1 has dark L_b diabatic state character and S_2 has bright L_a diabatic state character. The two excited states were optimized starting from the FC point. The S_1 and S_2 states were found to have the same L_b and L_a diabatic state characters at the ground state, S_1 and S_2 minimum energy structures and at the MECI between the S_1 and S_2 states. The molecular orbitals involved in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions at the critical point structures have been included in Section I of the SI. The comparison between vertical excitation energies and absorption spectra at the TDA/PBE0 level with experimental results has been included in Section I of the SI as well.

2.3.2 NAMD Trajectory Analysis

An ensemble of $n_{\text{traj}} = 40$ trajectories was propagated for $T = 2000$ time steps (corresponding to 1 ps) after initial excitation to the S_2 state. Starting on the S_2 state, pyrene quickly populated the S_1 state, while the S_2 population decayed exponentially with a lifetime of 40 fs (Table 2.1). This is comparable to the experimental lifetime of 85 fs computed using transient absorption spectroscopy [85]. After the $S_2 \rightarrow S_1$ relaxation, the further transfer to the S_0 state was too slow to produce reliable statistics. The experimental lifetime of the S_1 state of pyrene measured in degassed solvent was found to be 354 ns [86]. However, two separate regions of the S_1 PES could be identified in the simulations based on the comparison of the oscillator strengths f_1 and f_2 of the S_1 and S_2 states, respectively. The structures with $f_1 < f_2$ were considered as having L_b (dark) character [83], while the structures with $f_1 \geq f_2$ were assigned to the L_a (bright) character. The transition dipole moment vectors of the structures with L_a character were found to be parallel to the short axis of the molecule, while the vectors of the structures with L_b character were parallel to the long axis of the molecule. The structures from the trajectories evolving on the S_2 state were found to have L_a character.

The S_1 state with dark L_b character predominated in the trajectory ensemble (94.83%, Table 2.1). The average occupation of the S_2 state was small (2.35%), reflecting the fast relaxation to the S_1 state. The trajectories also occupied the S_1 state with L_a character (0.91%). The remaining occupation can be attributed to a single trajectory which switched to the ground state after 600 fs (Figure 2.2, Table 2.1).

2.3.3 NAMD Fluorescence Spectrum

The spectrum exhibits two separate bands. The low-energy band (< 3.4 eV) is higher in intensity and is attributed to emission from the S_1 state with L_b character. The high-energy

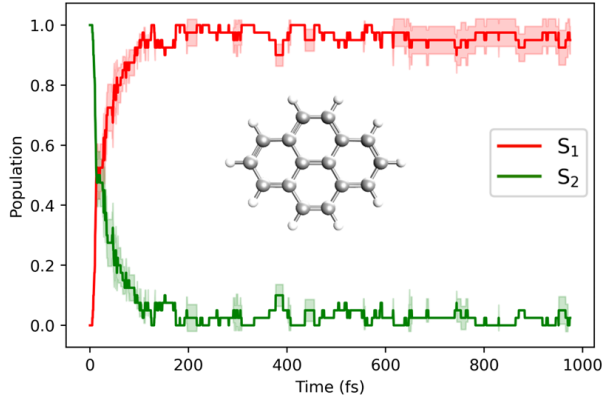
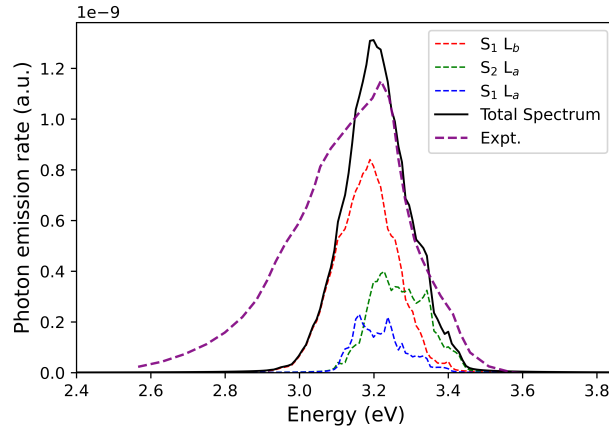


Figure 2.1: The population of the S_1 and S_2 states of pyrene as a function of time. The shaded regions indicate the 95% confidence intervals obtained by bootstrap resampling.

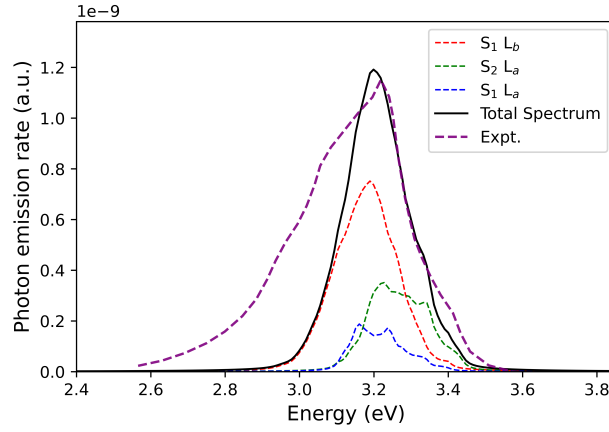
State m	$\bar{p}_m[\%]$	$\bar{E}_m$, eV	$\bar{f}_m$
S_2	2.35	3.73	0.281
S_1 (L_a)	0.91	3.68	0.356
S_1 (L_b)	94.83	3.62	0.010
S_0	1.90	0.0	0.0

Table 2.1: State occupations, $\bar{p}_m$, average energies, $\bar{E}_m$, and oscillator strengths, $\bar{f}_m$, (length gauge) of the S_m , $m = 1, 2$, states of pyrene from NAMD simulations with $n_{\text{traj}} = 40$ trajectories and simulation time $T = 1$ ps after an equilibration period of 0.5 ps.

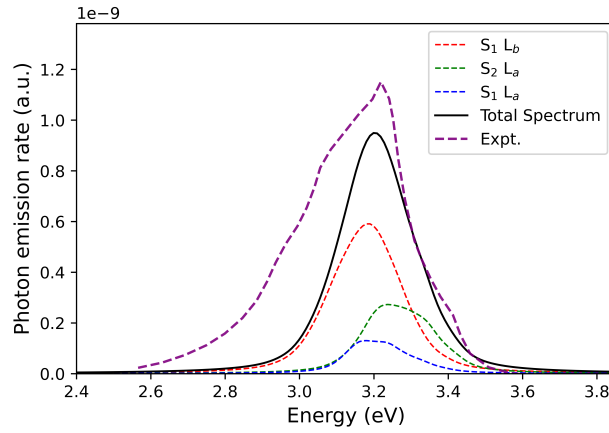
band (> 3.4 eV) contains emission from S_1 and S_2 states with L_a character (Figure 2.2). However, the thus obtained spectra depend on the lineshape function: Smaller linewidths lead to a distinct shoulder in the high-energy region but fail to reproduce the low-energy tail of the spectrum, whereas the high-energy shoulder is obscured when using larger linewidths that more adequately reproduce the width of the experimental spectrum. Although, NAMD accounts for anharmonicity to a certain degree the computed spectrum lacks the vibrational structure present in the experimental spectrum which is reproduced by the VPT S_1 (BO) spectrum (Figure 2.3).



(a)



(b)



(c)

Figure 2.2: Fluorescence emission spectrum of pyrene simulated by NAMD in comparison with experiment [1]. The relative experimental intensities were scaled to match the vibronic perturbation theory intensities, see Fig. 2.3. Lorentzian linewidths of (a) 0.005 eV, (b) 0.01 eV, and (c) 0.03 eV were used. All computed spectra were red-shifted by 0.45 eV to facilitate comparison with experiment.

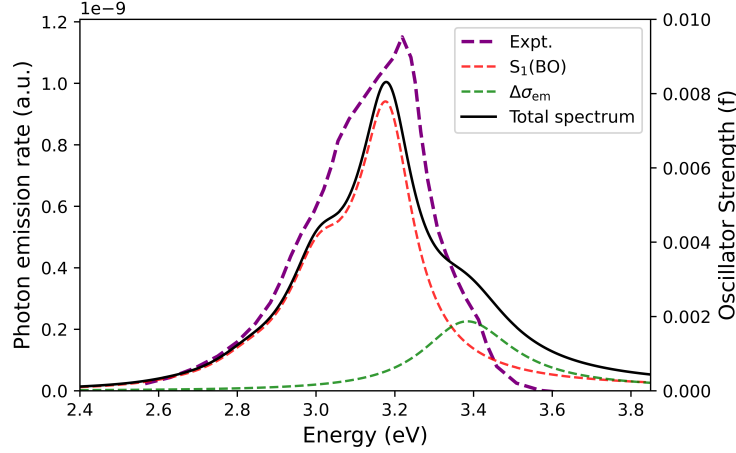


Figure 2.3: Fluorescence emission spectrum of pyrene obtained from vibronic perturbation theory in comparison with experiment [1]. The relative experimental intensities were scaled to match the computed intensities. The zero-order BO spectrum was determined by FC simulations using the generating function approach [2], whereas the FONAC correction $\Delta\sigma_{em}$ was simulated using a Lorentzian centered at the adiabatic S_2 excitation energy with a linewidth of 0.15 eV. All computed spectra were red-shifted by 0.45 eV to facilitate comparison with experiment.

2.3.4 Vibronic Perturbation Theory

The simulated fluorescence spectrum of pyrene using the vibronic perturbation theory expression, 2.4, is shown in Figure 2.3. The lower-energy band is due to FC transition from the relaxed S_1 state with L_b character. The adiabatic excitation energy of the S_1 state is $E_1^{\text{ad}} = 3.72$ eV, and the norm of electronic transition dipole moment is $|\mu_{01,\text{el}}| = 0.104$ a.u. The high-energy shoulder arises from the first-order correction $\Delta\sigma_{em}$ due to FONAC of the S_1 and S_2 states. The S_1 and S_2 states are coupled by a single “promoting” mode which is nearly parallel to the FONAC vector (Figure 2.4).

The S_2 emission energy is determined by computing the difference in energy between the initial and final vibronic levels of the S_2 and S_0 states, which is equal to the adiabatic excitation energy of the S_2 state is $E_2^{\text{ad}} = 3.86$ eV. The corresponding electronic transition dipole moment norm is $|\mu_{02,\text{el}}| = 1.778$ a.u. The magnitude of the Herzberg–Teller contribution terms $|\mu_{if}^{(0,1)}| = 0.0004$ and $|\mu_{if}^{(1,1)}| = 0.0002$ were found to be small in comparison to the

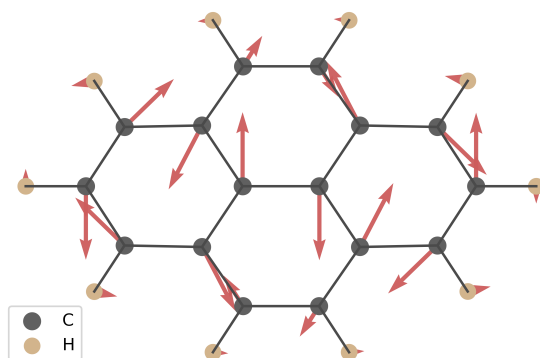


Figure 2.4: The promoting mode, i.e., the S_1 normal model with largest overlap with the S_1 - S_2 FONAC vector. Displacements are indicated by arrows. All displacements are in the molecular plane.

FONAC terms $|\boldsymbol{\mu}_{if}^{(1,0)}| = 0.05$, due to the weak dependence of the electronic transition dipole moments of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions on the nuclear coordinates. The S_1 (BO) contribution of VPT spectrum includes the vibrational structure of the spectrum computed using the harmonic approximation (FC spectrum). Due to the limitations of the current implementation of VPT, the $\Delta\sigma_{\text{em}}$ contribution to the spectrum does not include the computation of the vibrational structure and instead the S_2 adiabatic excitation energy is used as an approximation to the emission energy. The full set of simulation results is presented in the Section III of the SI.

2.3.5 Intersection Space

The energetic and emission parameters of the S_1 and S_2 states of pyrene in the intersection space are shown in Figure 2.5. The changes in the oscillator strengths illustrate that the character of the S_1 state switches from dark L_b to bright L_a and vice versa for the S_2 state. Due to the rigidity of the pyrene molecule, the minimum-energy structures of the excited S_1 and S_2 states, as well as the S_0 ground state (FC point), exhibit a high degree of structural similarity. The MECI structure lies 0.12 eV higher than the S_1 energy minimum and 0.01 eV

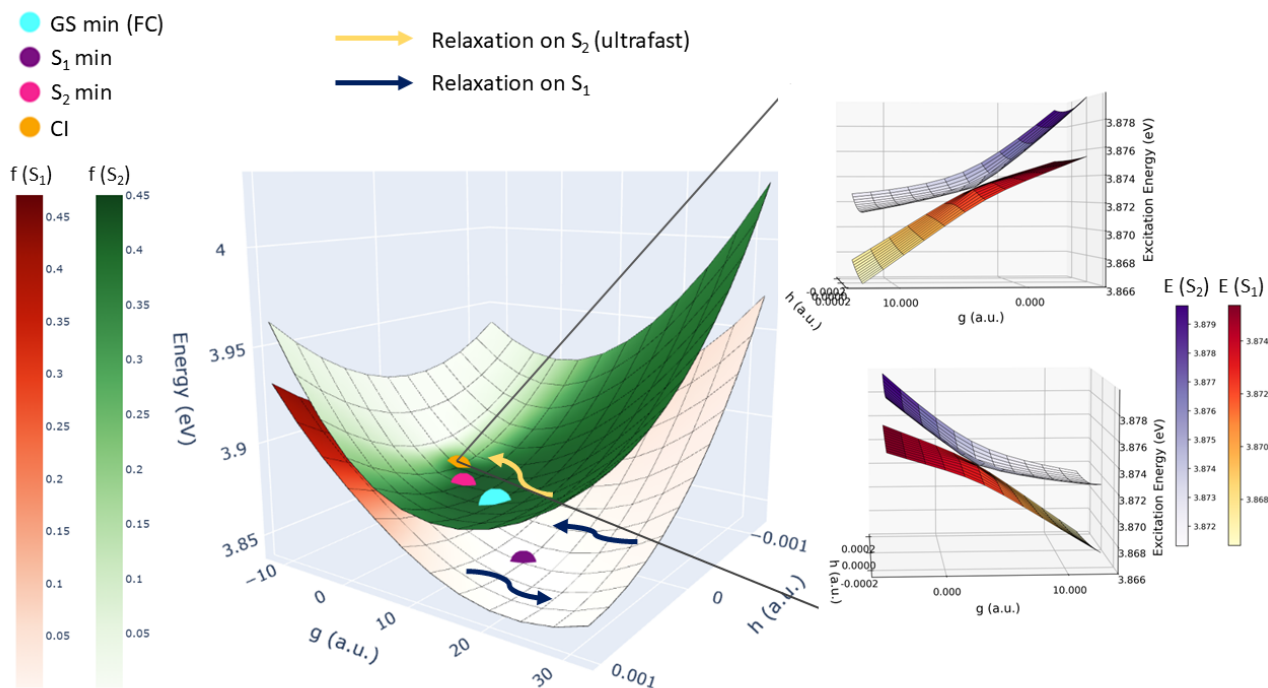


Figure 2.5: Energies of the S_1 and S_2 excited states of pyrene in the intersection space around the S_1/S_2 minimum energy conical intersection (MECI). The projections of the S_0 energy minimum (FC point), S_1 , S_2 energy minima energy structures, and the MECI point are shown. Insert: Enlarged view of the vicinity of the MECI, with energies the S_1 and S_2 states shown on a color scale.

higher than the S_2 minimum. Moreover, the FC point of the S_1 PES is only 0.08 eV above the MECI, see Table 2.2. The energy differences are approximately preserved in the intersection space, which indicates the two-dimensional representation captures the essential features of the full multidimensional PESs in the vicinity of the CI.

Structure	E_m [eV]	E'_m [eV]
FC	3.956	3.876
S_1 min.	3.752	3.845
S_2 min.	3.861	3.870
MECI	3.873	3.873

Table 2.2: Electronic energies, E_m , (eV) of the S_m , $m = 1, 2$ energy minima, the minimum energy conical intersection (MECI) point, and the FC point of pyrene and energies E'_m of the critical point projections on the intersection space. All energies are given relative to the ground-state S_0 minimum energy. No vibrational energy corrections were applied.

2.4 Discussion

The interpretation of the non-Kasha behavior of pyrene differ depending on the theoretical framework used. NAMD simulations of pyrene indicate that the high-energy shoulder in Figure 2.2 can be explained in terms of a reverse internal conversion $S_2 \rightarrow S_1$, as previously suggested by Barbatti and co-workers [21], but also as a result of the change in state character of the S_1 state between L_b (dark) and L_a (bright). As Table 2.1 shows, the average oscillator strength of the region of the S_1 PES with L_a character is comparable to that of the S_2 state, which results in a non-negligible contribution to the high-energy emission, see Figure 2.2. NAMD is suitable for simulating the non-Kasha behavior involving emission from multiple electronic states as it requires the description of several excited state transitions. Pure BO excited state MD is less suitable for this purpose as such simulations are restricted to the PES of a single electronic state and offers minor computational advantage.

Equilibrium response theory is generally far less computationally demanding than NAMD simulations. Approaches such as the FC and the Franck–Condon Herzberg–Teller (FCHT),

usually only include emission occurs from the lowest-lying electronic excited state. [51, 87, 88] The FCHT method additionally takes into account the variation of the transition moment with respect to nuclear displacements. However, the FC and FCHT do not adequately describe the vibronic effects in emission spectrum of pyrene.[14, 38] The present results show that vibronic perturbation theory provides an accurate description of the fluorescence spectrum of pyrene, including the high-energy shoulder, if (i) the HT couplings are accurately computed, (ii) the nonadiabatic coupling between the S_1 and S_2 states is included as an additional perturbation. The inference that FONAC terms dominate HT terms is only possible if the HT couplings are computed carefully. Implementations based on finite differences may provide erroneous results due to large default displacement size as demonstrated by the results of the numerical calculations in Section III of the SI. The correction to the transition dipole moment due to FONAC, $\mu_{if}^{(1,0)}$, is found to be 0.05 a.u. in magnitude, only slightly less than the zero-order BO S_1 transition dipole moment. The HT corrections are several orders of magnitude smaller.

2.5 Conclusions

Both NAMD and vibronic perturbation theory qualitatively capture the non-Kasha fluorescence of gas-phase pyrene. Strong nonadiabatic coupling between the S_1 and S_2 states is the origin of the non-Kasha fluorescence emission, even though the pictures emerging from both approaches appear very different: The vibronic calculations show clear evidence of “intensity stealing” by nonadiabatic mixing of the S_1 and S_2 BO states: Even at the S_1 equilibrium structure, the nonadiabatic coupling is strong enough to allow for virtual excitations into low-lying excited vibrational levels of S_2 which emit to the ground state. In the NAMD simulations, on the other hand, the CI between S_1 and S_2 is crucial for the non-Kasha emission, because it enables population transfer between the two BO surfaces. While the picture

emerging from the NAMD simulations is intuitively appealing, it does not imply that the non-Kasha fluorescence of pyrene is a fundamentally “dynamic” effect. Rather, our vibronic perturbation calculations suggest that the S_2 population observed in the semiclassical trajectory simulations mimics the vibronic mixing between the “static” nuclear wavefunctions of the two BO states.

Our results confirm semiclassical NAMD simulations as a valuable tool for mechanistic discovery, because they can be run with relatively little user input and will capture a wide variety of different mechanisms, at least if the timescale is short enough. Moreover, NAMD simulations are fundamentally capable of describing transient processes far from equilibrium. A major downside of NAMD simulations is their relatively high computational cost; also, the resulting spectra typically lack structure and may show incorrect intensities due to the use of semiclassical nuclei. The use of empirical lineshape functions is particularly problematic for pyrene, because the relatively small high-energy shoulder disappears from the NAMD spectrum for larger linewidths. Moreover, while including thermal effects in NAMD simulations is straightforward, it can be difficult to distinguish them from nuclear quantum effects, which are treated on the same footing within FSSH. While more sophisticated treatments of nuclear quantum effects [89, 90] may address these issues, they are even more resource-intensive than semiclassical NAMD.

Equilibrium response theory is much more confined in scope, but rather inexpensive compared to NAMD simulations when using electronic structure methods of similar complexity. In particular, the results of this work suggest that extending existing efficient approaches for the calculation of FC spectra [2, 51] to incorporate nonadiabatic effects may be worthwhile, particularly for the simulation of high-resolution steady-state spectra. Since NAMD simulations and vibronic perturbation theory are complementary, they can be synergistically combined in a two-step approach: NAMD simulations can be used initially to “scout” the potential energy surfaces and qualitatively identify key mechanisms and stationary points of

interest, followed by more refined vibronic calculations yielding accurate spectral intensities.

Chapter 3

Time resolved spectroscopic observables from non-adiabatic dynamics

This chapter contains verbatim excerpts from “J. Franzke, C. Holzer, J. H. Andersen, T. Begušić, F. Bruder, S. Coriani, F. Della Sala, E. Fabiano, D. A. Fedotov, S. Furst, S. Gillhuber, R. Grotjahn, M. Kaupp, M. Kehry, M. Krstić, F. Mack, S. Majumdar, B. D. Nguyen, S. M. Parker, F. Pauly, A. Pausch, E. Perlt, G. S. Phun, A. Rajabi, D. Rappoport, B. Samal, T. Schrader, M. Sharma, E. Tapavicza, R. S. Treß, V. Voora, A. Wodyński, J. M. Yu, B. Zerulla, F. Furche, C. Hättig, M. Sierka, D. P. Tew, and F. Weigend. TURBOMOLE: Today and tomorrow. *J. Chem. Theory Comput.*, 19(20):6859–6890, 2023.”

Author contribution of Sourav Majumdar : Contributed to the research discussed in section 3.10 and was involved in conceptualization (equal), execution (lead), and writing (equal).

3.1 Introduction

Recent methodological developments have made it possible to extract time-resolved spectroscopic observables directly from nonadiabatic molecular dynamics (NAMD) simulations. In particular, quadratic-response time dependent density functional theory (TDDFT) [5, 7, 67] enables the computation of transition dipole moments and nonadiabatic couplings between excited states, which are required for efficient simulation of excited state dynamics and the computation of time-resolved fluorescence (TRF) and transient absorption (TA) spectra. The implementation of multistate fewest-switches surface hopping (FSSH) [8] in TURBOMOLE [72, 73] extends these capabilities to systems containing 50–100 atoms over simulation times exceeding 10 ps.

This framework provides a powerful connection between theory and experiment, allowing simulated observables to be compared directly with ultrafast spectroscopic measurements. Such simulations can reveal the role of multiple electronic states, test the applicability of Kasha’s rule, and provide mechanistic insight into non-Kasha emission. In this chapter, we apply NAMD with quadratic-response TDDFT [7] to prototypical polycyclic aromatic hydrocarbons, including azulene, pyrene, and bicyclo[6.2.0]decapentaene (BCDP), to investigate their excited-state dynamics and associated time-resolved spectra.

3.2 Computational Methodology

Initial conditions for the NAMD simulations were sampled from a 10 ps long ground-state *ab initio* molecular dynamics (AIMD) simulation. For AIMD simulations, the hybrid functional PBE0 [54] and the split-valence def2-SVP basis sets [69] were used. The molecular dynamics were propagated using the Verlet–leapfrog algorithm with a time step of 20 a.u. (≈ 0.5 fs). Geometries and velocities for initiating NAMD simulations were obtained by

uniform sampling from the AIMD trajectory after an equilibration period of 0.2 ps

For electronic structure calculations in NAMD simulations using density functional theory (DFT), the hybrid functional PBE0 [54], which is known to be accurate for excited states of PAH molecules [65], together with D3-dispersion corrections [74], was used for all calculations. The def2-SVP basis set [69] was employed for all atoms. Excited states were computed using time-dependent density functional theory (TDDFT) with the Tamm–Dancoff approximation (TDA) [59] to avoid numerical instabilities. The nonadiabatic couplings between ground and excited states [52] were computed using linear-response TDDFT, while couplings between excited states [7] were obtained using quadratic-response TDDFT [67]. For each molecule, a swarm of NAMD trajectories was initiated from the excited state with the highest oscillator strength in the UV–vis region. Spectroscopic observables were computed by ensemble averaging over this set of trajectories. The time-resolved fluorescence (TRF) spectrum was computed as follows,

$$I^{\text{TRF}}(\omega, t) = \frac{1}{n_{\text{traj}}} \sum_{i=1}^{n_{\text{traj}}} f_{k \rightarrow 0} \omega_{k \rightarrow 0}^2 g(\omega - \omega_{k \rightarrow 0}), \quad (3.1)$$

where state k is the active state at time t , n_{traj} is the total number of trajectories, ω and f are the corresponding excitation energies and oscillator strengths, and g is a Gaussian broadening function. The transient absorption (TA) spectrum was computed as follows,

$$I^{\text{TA}}(\omega, t) = \frac{1}{n_{\text{traj}}} \sum_{i=1}^{n_{\text{traj}}} \left[\sum_{j>a} |\mu_{a \rightarrow j}|^2 g(\omega - \omega_{a \rightarrow j}) - \sum_{k<a} |\mu_{k \rightarrow a}|^2 g(\omega - \omega_{k \rightarrow a}) \right], \quad (3.2)$$

where $\mu_{m \rightarrow n}$ is the transition dipole moment between states m and n , and g is a Gaussian

broadening function.

3.3 Results

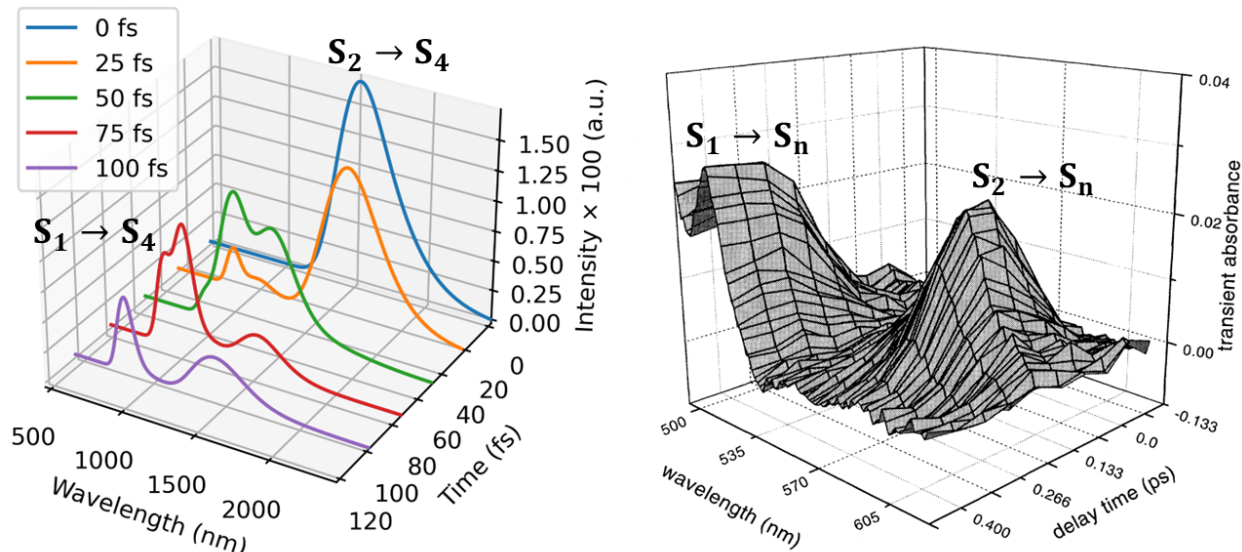


Figure 3.1: Computed (left) and experimental (right) TA spectra of pyrene in the gas phase. Band origins of S_1 and S_2 were shifted by -0.42 and -0.02 eV, respectively.

Multistate NAMD simulations were carried out at the PBE0/def2-SVP level of theory. The ability to simulate TRF and TA spectra enabled a direct comparison with experimental results (fig.3.1). Azulene exhibited clear non-Kasha behavior, with significant emission from the S_2 state. The computed S_1 lifetime of 2.2 ps and S_2 lifetime of 63 fs are in good agreement with the experimental values of 1.4 ps and 85 fs, respectively. In contrast, BCDP obeyed Kasha’s rule, fluorescing exclusively from the S_1 state with a lifetime of 0.8 ps. For pyrene, simulations revealed that the high-energy shoulder in the fluorescence spectrum originates from a change in diabatic character of the S_1 state from dark (L_b) to bright (L_a) at points of near-degeneracy with S_2 , combined with $S_1 \rightarrow S_2$ population transfer. The TA spectrum of

pyrene was also reproduced from ensemble-averaged NAMD trajectories. While the predicted absorption maxima ($\lambda(S_2 \rightarrow S_4) = 1500 \text{ nm}$, $\lambda(S_1 \rightarrow S_4) = 800 \text{ nm}$) are red-shifted relative to experiment, the time evolution of the signals and their assignment to specific excited-state transitions agree well with experimental measurements.

3.4 Conclusion

This study demonstrates that time-resolved spectroscopic observables can be reliably obtained from NAMD simulations using quadratic-response TDDFT. Both TRF and TA spectra of prototypical PAHs were simulated with quantitative accuracy in lifetimes and qualitative agreement in spectral features. Azulene shows non-Kasha fluorescence from S_2 , BCDP follows Kasha’s rule with S_1 emission, and pyrene exhibits mixed behavior due to diabatic state character changes.

The ability to compute spectroscopic signals directly from dynamics trajectories provides a powerful bridge between theory and experiment, enabling mechanistic interpretations of ultrafast measurements. These results highlight the potential of modern multistate NAMD methods to investigate complex nonadiabatic processes and to predict time-resolved observables in large molecular systems.

Chapter 4

Bioluminescence from ab-initio molecular dynamics driven by weighted ensemble simulations

Author contribution of Sourav Majumdar : Sourav Majumdar and Praveen Ranganath Prabhakar contributed equally to this work.

4.1 Introduction

Bioluminescence, the process by which living organisms convert chemical energy into light, represents one of the most striking examples of nature’s ability to harness reactive intermediates for functional photochemistry [91, 92]. At the core of this phenomenon lies *chemiexcitation*, the formation of electronically excited states through bond-breaking and bond-forming processes without external photo-excitation. Despite decades of experimental and theoretical investigations, the details of how specific bond rearrangements channel chemical energy

into the electronic excitation remain incompletely understood. In particular, the relative roles of the O-O and the C-C bond cleavage in strained dioxetanone intermediates, such as those present in dinoflagellate luciferin (**DL**), continue to be debated.

From a theoretical standpoint, simulating chemiexcitation is a formidable challenge. The reactive species are short-lived, highly strained, and often accessed only through rare conformational fluctuations that evade conventional ab initio molecular dynamics (AIMD). Furthermore, the dynamics involve multiple coupled potential energy surfaces, requiring explicit treatment of nonadiabatic transitions near conical intersections. Previous computational studies have offered useful insight into the mechanism of bioluminescence in DL and suggested possible bond cleavage pathways, but have often been restricted by limited sampling of rare geometries or by approximate treatments of the electronic structure [93–95].

Recent advances in rare-event sampling and trajectory-based nonadiabatic dynamics provide an opportunity to overcome these limitations. Weighted ensemble (WE) methods enhance sampling along chosen reaction coordinates by redistributing trajectory weights, enabling the capture of bond-breaking events inaccessible to conventional AIMD within feasible timescales. When combined with accurate excited-state electronic structure methods and trajectory-based approaches such as surface hopping, these methods allow direct simulation of the chemiexcitation process and the computation of associated spectroscopic observables.

In this work, we integrate WE-driven ground-state AIMD, nonadiabatic molecular dynamics (NAMD), and spectroscopic analysis to investigate the chemiexcitation of dinoflagellate luciferin. WE-driven AIMD with density functional theory provides reactive geometries at which O-O and C-C bond breaking occurs, identifying regions of the potential energy surface with a small energy gap between the ground state S_0 and the first singlet excited state S_1 . These geometries serve as initial conditions for nonadiabatic surface hopping trajectories, enabling us to simulate the $S_0 \rightarrow S_1$ population transfer. From these trajectories, we compute both steady-state and time-resolved bioluminescence spectra, which we compare to

experimental results. Our results demonstrate that the O-O bond cleavage is the initiating event, followed by C-C bond rupture, and these coupled motions funnel the system through conical intersections that efficiently populate the excited state, leading to bioluminescence.

The combined WE-AIMD-NAMD framework provides a tractable route to simulating *chemiexcitation* in complex systems. The present study thus serves as a proof of principle that weighted-ensemble AIMD combined with nonadiabatic dynamics can simulate challenging long-timescale processes and reproduce spectroscopic observables.

4.2 Theory

4.3 Computational Methods

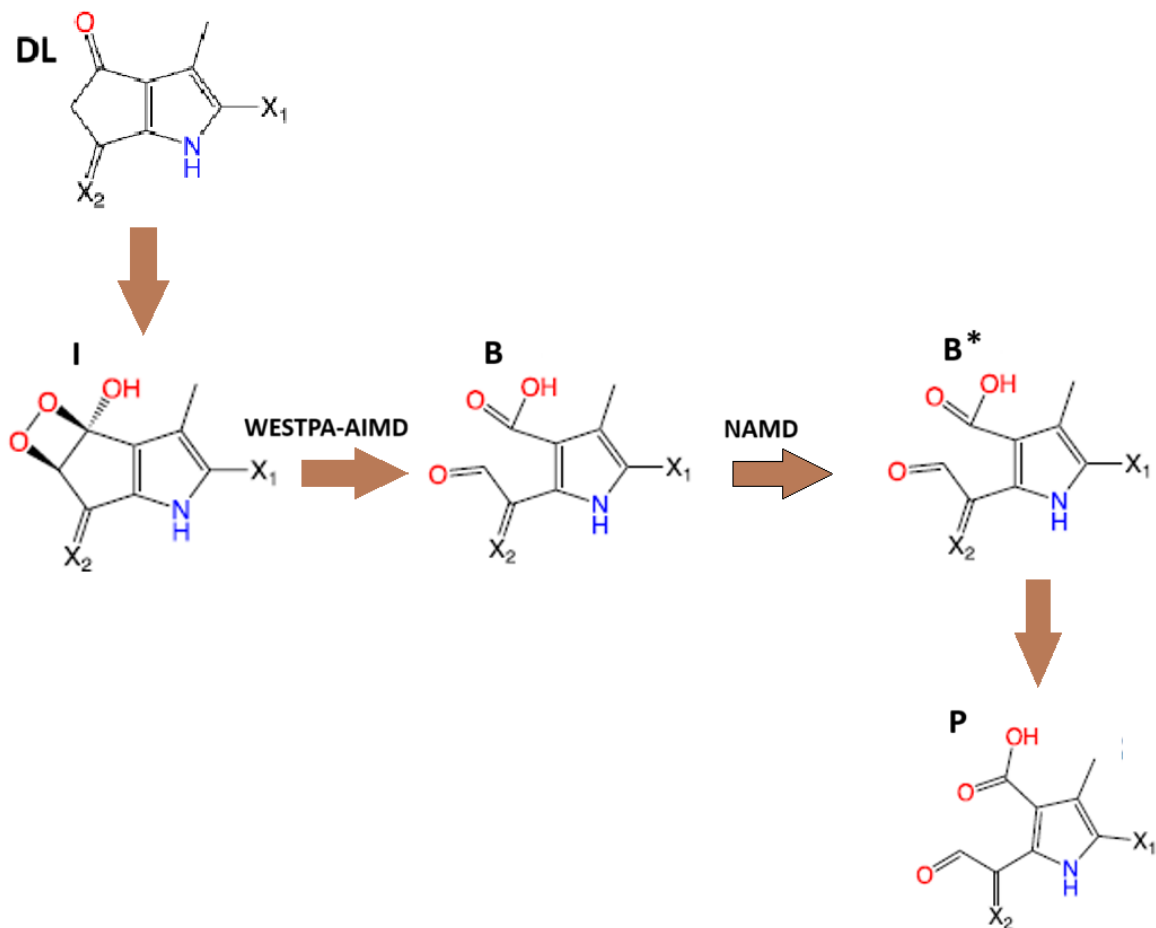


Figure 4.1: Schematic overview of the simulation workflow for chemiexcitation in dinoflagellate luciferin (DL), showing the progression from the intermediate (I) through the bioluminescent species (B) to the final product (P). Weighted-ensemble AIMD (WESTPA-AIMD) is used to sample bond-breaking events leading from I to B, and nonadiabatic molecular dynamics (NAMD) captures the chemiexcitation of B and the subsequent excited-state dynamics leading to P.

4.3.1 Ab-initio molecular dynamics driven by weighted ensemble simulations

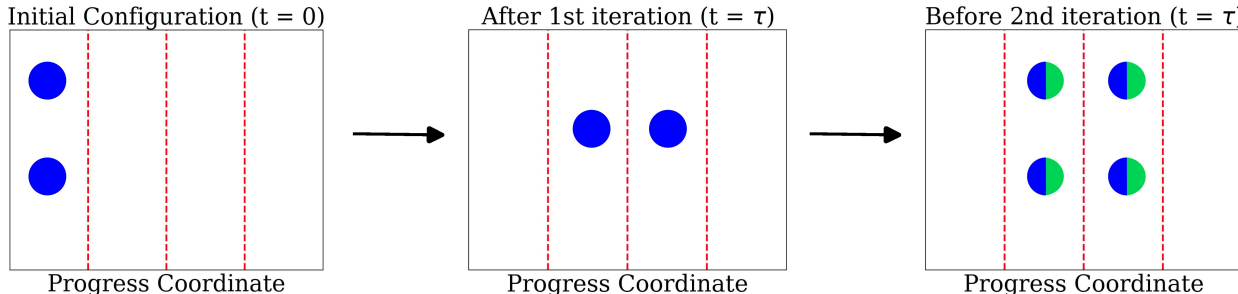


Figure 4.2: Principle of Weighted ensemble simulations

Ab-initio ground state molecular dynamics simulations were performed using spin-unrestricted density functional theory (DFT) with ω B97X-D [96] functional and def2-SVP [69] basis sets for all atoms. Solvent effects were modeled using the continuum solvation model COSMO [97] with a dielectric constant of 80.1 and a refractive index of 1.33 for water. DFT quadrature grids of size of m4 [98] were maintained throughout.

The optimized geometries of each of the four stereoisomers of the intermediate **I**[93] of **DL**[93, 95, 99] (fig.4.1), served as the initial structures for the ground-state molecular dynamics simulations. From the optimized structures, the WE simulations were initiated with 4 walkers per bin. A manual rectangular binning was implemented with the oxygen-oxygen bond distance of the four-membered ring as the progress coordinate. The bin definitions are provided in the SI. The resampling time was set to 5 fs per iteration. The simulations were performed at 400 K using a Nosé–Hoover thermostat [100, 101], and the trajectories were propagated using the leapfrog Verlet algorithm [71] with a time step of 40 a.u. $\approx$ 1 fs. The leapfrog Verlet algorithm implemented in Turbomole is deterministic and hence to introduce stochasticity in the dynamics, after every iteration, the velocities were randomly redistributed in accordance to the simulation temperature. The WE simulations were implemented in WESTPA 2.0 [102], and the ab-initio molecular dynamics was carried out with

the TURBOMOLE program suite, Version V7.5 [72, 73]. The WE simulations were stopped once sufficient structures for the excited state dynamics were obtained. The spin state is checked at the start of every iteration to ensure the ground state is preserved.

4.3.2 Non-adiabatic dynamics

Initial conditions for the NAMD simulations, involving the ground state (S_0) and the first singlet excited state (S_1), were derived from the weighted ensemble ground-state molecular dynamics trajectories, which exhibited bond cleavage. Consistent with prior computational studies, these bond-breaking conditions revealed a narrow energy gap of less than 0.5 eV between the S_0 and the S_1 potential energy surfaces (PESs). The initial geometries for the NAMD trajectories were sampled from the WE trajectories at the earliest point of time following bond breaking, where the expectation value of the spin operator was $\langle S^2 \rangle \approx 0$ to avoid spin contamination.

Non-adiabatic molecular dynamics (NAMD) simulations were performed using the fewest switching surface hopping (FSSH) method using spin restricted DFT with the ω B97X-D3 functional [103]. Excitation energies and excited-state gradients were computed using the Tamm–Dancoff approximation (TDA) [59, 62, 63] to time-dependent density functional theory (TDDFT). The def2-SVP [69] basis sets were used for all atoms and the solvent effects for water were modeled using the continuum solvation model conductor-like polarizable continuum model (CPCM) [104]. The non-adiabatic couplings were computed using the time-dependent Baer–An approach [105] and the trajectories were propagated using the velocity Verlet algorithm [71] with a time step of 8 a.u. $\approx$ 0.2 fs. A swarm of 200 trajectories, comprising of 50 trajectories from each stereoisomer and initialized with randomized velocities [106], was propagated for a total duration of 0.5 ps. Electronic structure calculations were performed using the ORCA [80] quantum chemistry package, while nonadiabatic dynamics simulations were carried out with the NEWTON-X program [9].

4.3.3 Trajectory analysis and computation of spectroscopic observables

The electronic properties of a trajectory at any specific time are defined by a single Born–Oppenheimer (BO) electronic state, designated as the active state. The time-dependent population $p_m(t)$ of an electronic state S_m was calculated based on the proportion of trajectories with active state m at time t . The 95% confidence intervals for the state populations were computed using bootstrap resampling with 50,000 samples [7, 76].

Spectroscopic observables were obtained by ensemble averaging over the entire set of trajectories. The steady-state bioluminescence spectrum was constructed from the NAMD simulations using the following lineshape function [107],

$$\sigma_{em}(\omega) = \frac{1}{N_{\text{steps}}} \sum_{j=1}^{N_{\text{steps}}} f_{j,a} \omega_{j,a}^2 G(\omega_{j,a} - \omega) \quad (4.1)$$

where $f_{j,a}$ is the oscillator strength of the active state a of the trajectory, ω is the excitation energy, N_{steps} is the total number of time steps from the trajectories after the equilibration period, and G is a Gaussian broadening function. Whereas the time-resolved bioluminescence spectrum was computed using the following lineshape function,

$$I(\omega, t) = \frac{1}{N_{\text{traj}}} \sum_{j=1}^{N_{\text{traj}}} f_{j,a}(t) \omega_{j,a}(t)^2 G(\omega_{j,a} - \omega) \quad (4.2)$$

where N_{traj} is the total number of trajectories. Further details about the computational methodology have been provided in Section I of the supporting information (SI).

4.4 Results

4.4.1 Weighted ensemble molecular dynamics

The WESTPA ground-state MD simulations were initiated from the optimized geometries of the isomers of intermediate **I**. The O–O bond in the four-membered ring was the first to break, driving the system into a diradicaloid state with $\langle S^2 \rangle \approx 1$. Trajectories exhibiting O–O bond cleavage also showed subsequent C–C bond breaking accompanied by the shortening of the C–O bonds, occurring shortly after the O–O rupture and almost simultaneously with $\langle S^2 \rangle$ coming back to ≈ 0 . These concerted bond-rearrangement events consistently coincide with a significantly reduced S_0 – S_1 energy gap (0.15–0.8 eV), indicating the presence of a conical intersection nearby on the potential energy surface (PES). At all times along the trajectories, when the molecule is not in a diradicaloid state, the smallest S_0 – S_1 energy gaps occurred at these geometries, which were subsequently chosen as the initial conditions for the NAMD simulations of the chemiexcitation process.

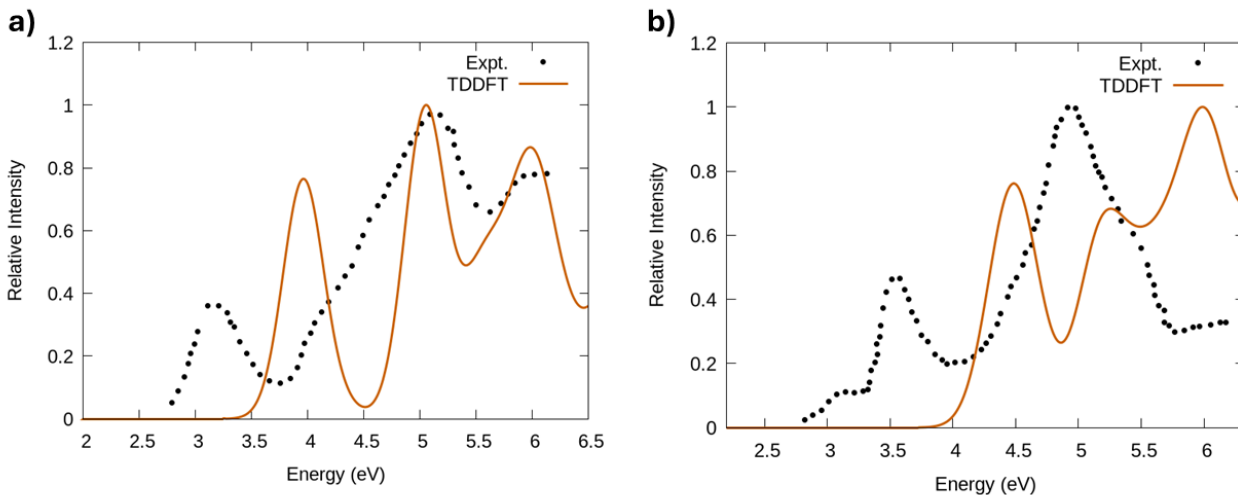


Figure 4.3: Experimental and simulated absorption spectra of a) **DL** and b) **P**, computed using TDDFT with ω B97X-D functional and def2-SVP basis sets. Gaussian broadening of 0.2 eV was employed, and the simulated spectrum was red-shifted by 0.2 eV for comparison with experiment for comparison with experiment.

4.4.2 Absorption spectra - initial and optimized broken structure

The absorption spectra of dinoflagellate luciferin (**DL**) and its oxidized final product (**P**) (fig.4.1) were computed at their ground state optimized geometries using TDDFT. A Gaussian lineshape with a 0.15 eV linewidth and an empirical red shift of 0.2 eV were applied to facilitate comparisons with experiment. The simulated spectra of **DL** and **P** show good agreement with the experimental spectrum, with the predominant peaks accurately reproduced (fig.4.3).

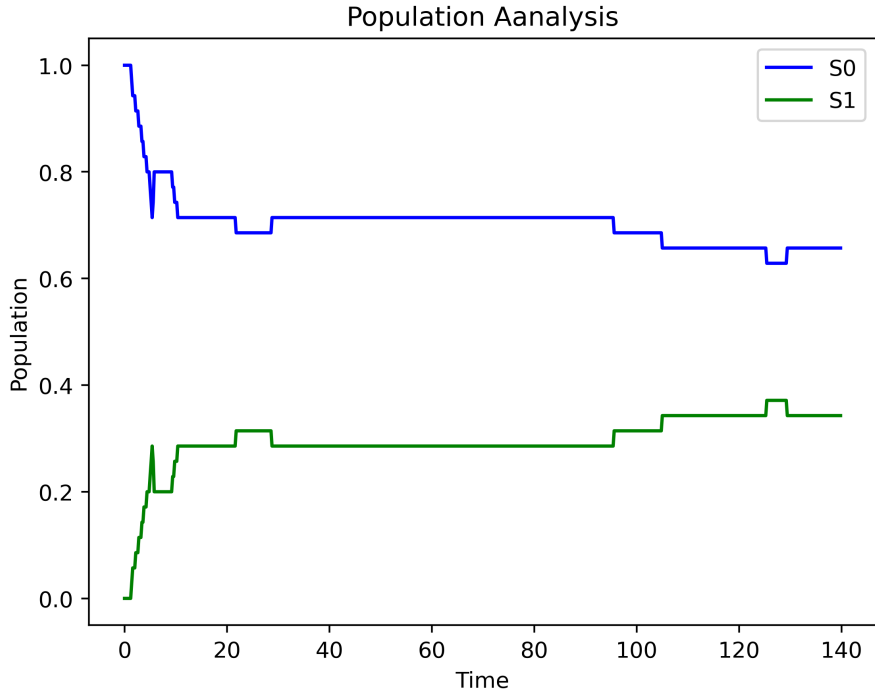


Figure 4.4: Population analysis of the NAMD trajectories initiated from **B** demonstrating the ultrafast $S_0 \rightarrow S_1$ population transfer and the subsequent steady state dynamics.

4.4.3 Chemiexcitation and bioluminescence

An ensemble of NAMD trajectories ($n_{\text{traj}} = 40$), was propagated for $T = 2500$ time steps (corresponding to 0.5 ps) after being initiated on the S_0 state. Starting on the S_0 state, about 30% of the trajectories exhibit transition to the S_1 state within the first 20 – 30 fs, after

which the populations of the S_0 and S_1 states remain constant (fig.4.4) as the trajectories move further away from the region of strong coupling near the CI towards **B** (fig.4.1). The further transition of the trajectories on the S_1 state to the S_0 state was too slow to produce reliable statistics. The steady state and time resolved bioluminescence spectra were computed using the excitaton energies and oscilaator strengths of the NAMD trajectories evlolving on the S_1 state with the help of eq 1 and 2. The steady state spectrum exhibits a single band centered at ≈ 2.5 eV in agreement with experimental results (fig.4.5). The time-resolved bioluminescence spectrum exhibits steady-state oscillations after the initial ultrafast chemiexcitation process (fig.4.6).

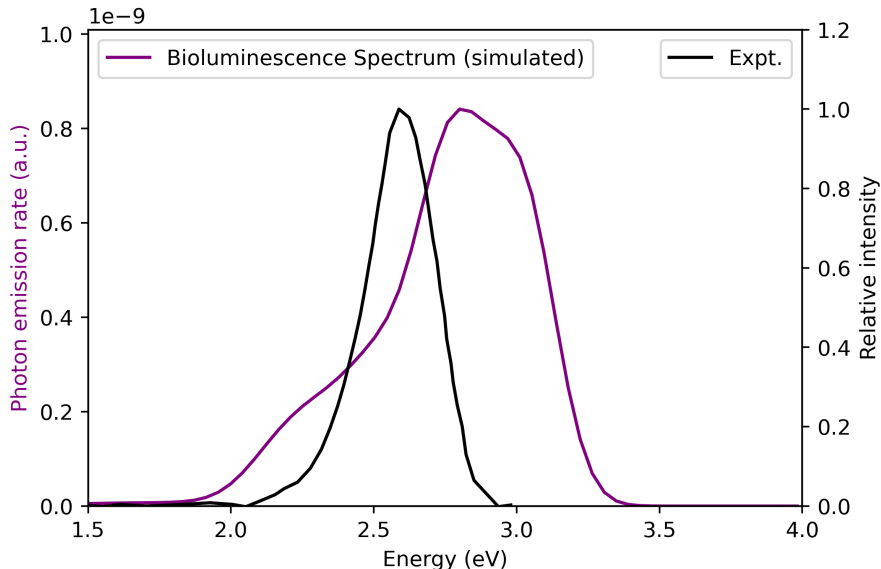


Figure 4.5: Steady state bioluminescence spectrum of dinoflagellate luciferin computed from the NAMD trajectories using a Gaussian lineshape function of linewidth 0.1 eV (More data and equilibration is required). The simulated spectrum was red-shifted 0.2 eV for comparison with experiment.

4.5 Discussion

Previous studies have firmly established that O–O bond cleavage occurs during the reaction [93–95, 99], motivating its selection as the primary reaction coordinate in the WESTPA

simulations. Weighted-ensemble ground-state MD confirms this choice, showing O–O bond rupture in the strained four-membered ring as the initiating step, driving the system into a diradicaloid configuration ($\langle S^2 \rangle \approx 1$). While the role of the C–C bond has been less certain [93, 95, 99], our results, consistent with recent computational studies [93], show that C–C bond breaking follows shortly after O–O cleavage, accompanied by C–O bond shortening and spin re-pairing ($\langle S^2 \rangle \rightarrow 0$). These bond-breaking geometries coincide with a narrowed S_0 – S_1 gap (0.15–0.8 eV), indicative of a nearby conical intersection which facilitates the $S_0 \rightarrow S_1$ population transfer. Furthermore, the structures of I,B and P have the C nuclei attached to the rest of the molecule, which explains why no CO_2 is released when the 4-member ring cleavage occurs and confirms that decarboxylation is not necessary for chemiexcitation.

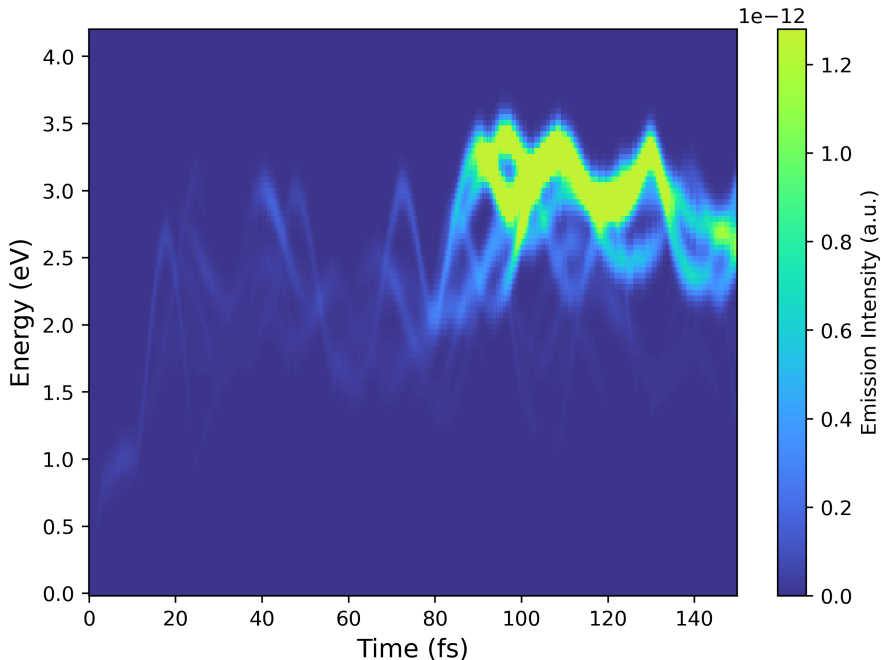


Figure 4.6: Time-resolved bioluminescence spectrum of dinoflagellate luciferin computed from the NAMD trajectories using a Gaussian lineshape function of linewidth 0.1 eV (More data and equilibration is required). The simulated spectrum was red-shifted 0.2 eV for comparison with experiment

Nonadiabatic dynamics from these WE-identified structures capture an ultrafast $S_0 \rightarrow S_1$ population transfer within 20–30 fs, after which the state populations remain constant as

trajectories evolve away from the CI region. The computed steady-state bioluminescence spectrum displays a single band near ~ 2.5 eV, in good agreement with experiment, and the time-resolved spectrum reveals sustained oscillations following the initial excitation.

Weighted-ensemble sampling is essential for capturing these rare, reactive geometries that would be inaccessible to conventional ab-initio MD. The combination of accurate ground-state DFT with TDA-TDDFT excited-state dynamics and an efficient surface hopping scheme provides a tractable approach that reproduces experimental observables while elucidating the nuclear motions that drive chemiexcitation. Future work will examine explicit solvent effects, alternative methods for computing non-adiabatic coupling, and chemical modifications to modulate the O-O/C-C coordinates and tune the S_0 - S_1 energy gap and chemiexcitation yield.

4.6 Conclusion

This work demonstrates that weighted-ensemble driven path sampling coupled with ab-initio ground state and nonadiabatic molecular dynamics simulation to provide direct access to the rare bond-breaking geometries that drive chemiexcitation in dinoflagellate luciferin. The computed bioluminescence spectra show excellent agreement with experiments and is consistent with the findings from earlier computational studies, and thereby validating the method as a predictive tool. More broadly, the WE-AIMD-NAMD framework offers a generalizable strategy for simulating long-timescale processes and excited-state dynamics in complex photochemical systems, bridging the gap between electronic-structure accuracy, rare-event sampling, and experimentally measurable observables.

Chapter 5

Quantum chemistry in collaboration with experiment

This chapter contains verbatim excerpts from “C. A. Goodwin, S. R. Ciccone, S. Bekoe, S. Majumdar, B. L. Scott, J. W. Ziller, A. J. Gaunt, F. Furche, and W. J. Evans. 2.2.2-Cryptand complexes of neptunium(III) and plutonium(III). *Chem. Commun.*, 58(7):997–1000, 2022.” , and

“K. C. Kenney, T. P. LaFortune, S. Majumdar, E. M. Manríquez, A. S. Pamidi, C. S. Kom, J. E. Garrido, E. S. Villa, F. Furche, and G. A. Weiss. Experimental and computational evaluation of nicotinamide cofactor biomimetics. *ACS Chem. Biol.*, 2025.”

Author contribution of Sourav Majumdar : Sourav Majumdar performed the electronic structure calculations and contributed to analyzing and writing the results.

5.1 Introduction

Quantum chemical methods have become indispensable tools for probing the structure and reactivity of complex molecular systems. Their ability to accurately compute molecular properties, energetics, and spectroscopic observables makes them highly complementary to experimental studies. In this chapter, we apply density functional theory (DFT) and time-dependent density functional theory (TDDFT) to two distinct but related problems: (i) the conformational dependence of oxidation potentials in nicotinamide cofactor biomimetics (NCBs), and (ii) the electronic absorption spectra of actinide cryptand complexes. These studies highlight how computational chemistry can provide mechanistic insight and quantitative support for experimental observations.

5.2 Method

5.2.1 Methodology for conformer search and calculation of reaction free energy of nicotinamide cofactors

Density functional theory (DFT) was used for all electronic structure calculations. Initial conformer searches and structure optimizations were performed using the TPSS functional [108] and the def2-SV(P) basis set [69]. Final reaction enthalpies were calculated using the TPSSh functional [109] with the def2-TZVP basis set [69]. Grimme’s D3 dispersion correction [55] was applied in all calculations. Solvent effects were modeled using the continuum solvation model COSMO [97] with a dielectric constant of 78.4 and a refractive index of 1.33 for water. DFT quadrature grids of size 4 were used throughout [98]. Standard Gibbs free energies were evaluated within the rigid-rotor harmonic-oscillator approximation. All computations were performed using the TURBOMOLE program suite, version 7.5 [72, 73].

For each molecular species, an ensemble of conformers was generated using the genetic algorithm implemented in the OPEN BABEL software package [110]. The generated conformers were subsequently optimized at the TPSS/def2-SV(P) level of theory. This process was iteratively repeated with increasing numbers of conformers until convergence was achieved.

5.2.2 Methodology for computation of absorption spectra of Actinide complexes

Electronic structure calculations on $[\text{An}(\text{crypt})\text{OTf}_2]^{3+}$ ($\text{An} = \text{U}, \text{Np}, \text{Pu}$) were carried out at the density functional theory (DFT) level using the TPSSh functional [109] with Grimme’s D3 dispersion correction [55] in C_1 symmetry. Scalar relativistic effective core potentials (ECPs) [111] with the def-SV(P) basis set were employed for the actinide centers, while polarized split-valence basis sets with diffuse functions (def2-SV(P)) [112] were applied to lighter atoms. DFT quadrature grids of size 4 were used throughout.

Solvent effects were included using the COSMO continuum solvation model [97] with dielectric constant $\epsilon = 7.5$ and refractive index $n = 1.3$, corresponding to tetrahydrofuran (THF) [113]. Geometry optimizations were performed starting from the corresponding X-ray structures without symmetry constraints, employing convergence thresholds of 10^{-4} a.u. for gradients and 10^{-7} a.u. for total energies. Optimized structures were verified as minima on the potential energy surface via vibrational analysis using finite-difference gradients.

Vertical excitation energies and oscillator strengths were computed within the time-dependent DFT (TDDFT) framework using def2-SVPD basis sets for ligands [70] and def-SV(P) for Pu and Np. Simulated UV–vis–NIR spectra employed Gaussian line shapes with a root mean-square width of 0.1 eV. Molecular orbitals, electronic states, and transitions were visualized using VMD [114] and further analyzed by Mulliken population analysis (MPA).

All calculations were carried out using the TURBOMOLE program suite, Version 7.5 [72, 73].

5.3 Results

5.3.1 Oxidation Potentials of NCBs

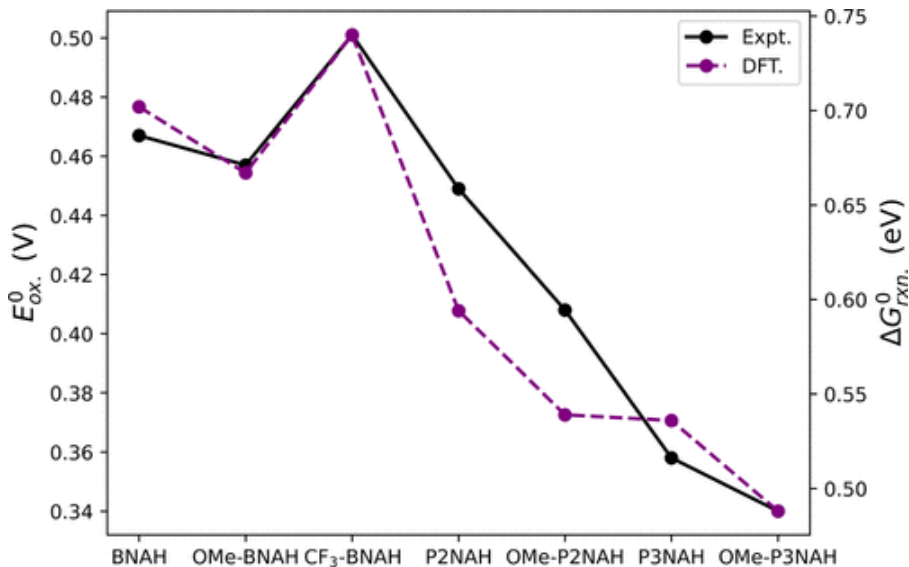


Figure 5.1: Comparison of the trends in experimental oxidation potential E_{ox}^0 (V) with the computed free energy change ΔG_{rxn}^0 (eV) upon oxidation and loss of a hydride ion for a range of NCBs investigated in the present study.

The conformers of NCBs with two- or three-carbon atoms in the linker chain (e.g., P2NAH, P3NAH, and their derivatives) exhibited surprisingly close nicotinamide to Ring 2 distances of 3.5–4.2 Å. The Gibbs free energy for the reaction corresponding to the oxidation of the NCBs and the loss of a hydride ion were calculated using these minimum-energy conformers. The computed free energy trends aligned with the experimentally observed oxidation potential trends for the NCBs (fig.5.1). Here, the free energy of the half-reaction for oxidizing the NCB is identical for all molecular species investigated. The oxidation potential variation

from BNAH to OMe-BNAH and CF₃-BNAH can be attributed to the electron-donating or electron-withdrawing effects of the substituents. However, understanding the changes in oxidation potential associated with NCBs having extra carbon atoms in their linkers required further analysis.

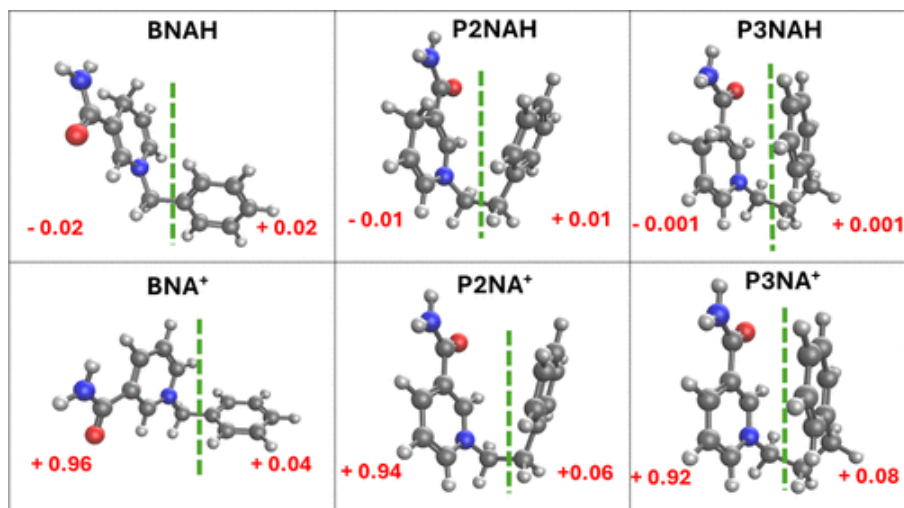


Figure 5.2: Natural bond orbital (NBO) population analysis of reduced and oxidized NCBs with varying lengths of linker. BNAH, P2NAH and P3NAH illustrate charge transfer facilitated by $\pi - \pi$ interactions. The green dashed line indicates the charge separation (numbers in red) between the left and right halves of each NCB.

The oxidation of the NCB and the hydride ion loss render the nicotinamide ring positively charged. Natural Bond Orbital (NBO) analysis of atomic partial charges revealed charge transfer between the nicotinamide and benzene rings upon oxidation (fig.5.2). Notably, the magnitude of charge transfer increased progressively from BNAH to P2NAH to P3NAH, in correlation with the decreasing inter-ring distance. The trend of decreasing oxidation potential with increasing linker chain length can be explained by intramolecular $\pi - \pi$ interactions: the increased conformational flexibility and longer linker length enables the nicotinamide and Ring 2 to stack more closely. The resulting π stacking interactions can donate charge stabilization to the oxidized species by partial charge transfer.

5.3.2 Absorption spectra of Actinide complexes

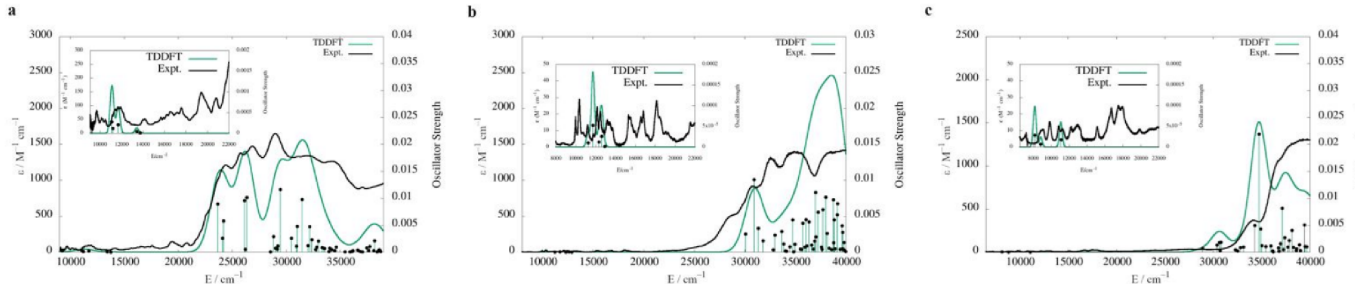


Figure 5.3: Black lines show solution UV-vis-NIR spectra of (a) $[\text{U}(\text{crypt})(\text{OTf})_2][\text{OTf}]$ (1-U, 5 mM), (b) 1-Np (1.89 mM), and (c) 1-Pu (2.05 mM) in THF at ambient temperature. Green lines show simulated UV-vis-NIR spectra of (a) $[\text{U}(\text{crypt})(\text{OTf})_2]^{1+}$, (b) $[\text{Np}(\text{crypt})(\text{OTf})_2]^{1+}$, and (c) $[\text{Pu}(\text{crypt})(\text{OTf})_2]^{1+}$ with computed TDDFT oscillator strengths shown as vertical lines. The experimental spectrum is shown in black for comparison. A Gaussian line broadening of 0.10 eV was applied. The computed intensities were scaled to ease comparison with the experimental spectrum.

TDDFT calculations of the simulated UV-vis-NIR spectra are shown in fig.5.3. For all three complexes $[\text{U}(\text{crypt})(\text{OTf})_2]^{1+}$, $[\text{Np}(\text{crypt})(\text{OTf})_2]^{1+}$, and $[\text{Pu}(\text{crypt})(\text{OTf})_2]^{1+}$, the calculations indicate very weak $5f \rightarrow 5f$ transitions in the 7000–20 000 cm^{-1} region and intense $5f \rightarrow 6d$ transitions at energies above 20 000 cm^{-1} . Although scalar relativistic DFT calculations do not provide accurate estimates of the intensity and splitting patterns of the $5f \rightarrow 5f$ transitions, the overall match of the UV-visible spectra in the $5f \rightarrow 6d$ region, and the absence of $6d \rightarrow 7p$ transitions (characteristic of divalent actinide compounds with $6d^1$ ground states) supports the assignment of $5f^n$ ground states with no $6d$ occupation.

The onset of $5f \rightarrow 6d$ transitions occurs at higher energies in the order $\text{U} < \text{Np} < \text{Pu}$, consistent with the increasing stabilization of the $5f$ manifold relative to the $6d$ orbitals as the actinide series is traversed from U to Np to Pu. Since TDDFT excitation calculations are susceptible to spurious charge transfer excitations from weakly bound anions, the spectra were also modelled with triflate-free cations $[\text{An}(\text{crypt})]^{3+}$. However, the $[\text{An}(\text{crypt})(\text{OTf})_2]^{1+}$ calculations provided the better match and are shown here.

5.4 Conclusion

This chapter demonstrates the utility of modern quantum chemical approaches in guiding and interpreting experimental research. For nicotinamide cofactors, conformer-dependent free energy calculations and charge analysis revealed how linker length and substituents modulate oxidation potentials through intramolecular π - π interactions and charge transfer. For actinide cryptate complexes, TDDFT calculations reproduced the main spectral features of the $5f \rightarrow 6d$ excitations, validating the assignment of $5f^n$ ground states and rationalizing trends across U, Np, and Pu. Together, these results underscore the value of electronic structure theory in establishing structure-property relationships and in offering predictive insight for experimental systems.

Chapter 6

Conclusion

This dissertation demonstrates concrete advances in bridging electronic structure theory with experimentally measurable spectra by addressing specific limitations of current methodologies. In particular, vibronic perturbation theory (VPT) was extended and validated as a practical tool for computing fluorescence spectra, overcoming the inability of conventional Franck–Condon approaches to capture deviations from Kasha’s rule. Coupled with nonadiabatic molecular dynamics (NAMD), this provides a systematic two-step protocol for simulating steady-state fluorescence in molecular systems. With these tools in place, one can now approach the prediction of vibronic effects in the absorption and fluorescence spectra of molecular systems.

The development of a framework to compute time-resolved spectroscopic observables, particularly transient absorption spectra, directly from multi-state NAMD simulations represents another step forward. This methodology allows one not only to reproduce ultrafast pump–probe experiments, but also to probe mechanistic details of excited-state relaxation that are otherwise inaccessible. Applications of this approach include disentangling photochemical pathways such as photostability of nucleobases.

The integration of weighted-ensemble *ab initio* molecular dynamics with NAMD provides, for the first time, a tractable way to capture rare long-timescale events such as chemiexcitation and bioluminescence. In the case of dinoflagellate luciferin, this framework reproduced both spectral signatures and mechanistic pathways, offering a generalizable strategy that can now be extended to other long timescale photochemical processes. Similarly, the carefully benchmarked DFT/TDDFT studies of nicotinamide cofactors and actinide cryptates showed that when protocols are chosen systematically, theoretical calculations can accurately predict redox potentials and absorption spectra, enabling direct guidance for experimental design.

Taken together, these methodological contributions shift the landscape from qualitative descriptions toward quantitative prediction of excited-state observables. They provide a roadmap: to simulate fluorescence, one can now employ VPT+NAMD protocols; to compute transient absorption, one can extract observables from multi-state NAMD; to model rare-event excited-state processes, weighted-ensemble dynamics can be applied. These tools open the door to specific applications such as rational design of fluorescent probes, mechanistic elucidation of chemiexcitation in living systems, and interpretation of actinide spectroscopy. In doing so, they advance the field toward the long-standing goal of using quantum chemical methods not only to rationalize experimental spectra, but also to predict new phenomena and guide experimental discovery.

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