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Towards Prediction of Non-Radiative Decay Pathways in Organic Compounds I: The Case of Naphthalene Quantum Yields

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Abstract

Many emerging technologies depend on human's ability to control and manipulate the excited-state properties of molecular systems. These technologies include fluorescent labeling in biomedical imaging, light harvesting in photovoltaics, and electroluminescence in light-emitting devices. All of these systems suffer from non-radiative loss pathways that dissipate electronic energy as heat, which causes the overall system efficiency to be directly linked to quantum yield (Φ) of the molecular excited state. Unfortunately, Φ is very difficult to predict from first principles because the description of a slow non-radiative decay mechanism requires an accurate description of long-timescale excited-state quantum dynamics. In the present study, we introduce an efficient semi-empirical method of calculating the fluorescence quantum yield (Φ_{fl}) for molecular chromophores, which converts simple electronic energies computed using time-dependent density functional theory (TDDFT) into an estimate of Φ_{fl}. As with all machine learning strategies, the algorithm needs to be trained on fluorescent dyes for which Φ_{fl}'s are known, so as to provide a black-box method which can later predict Φ's for chemically similar chromophores that have not been studied experimentally. As a first illustration of how our proposed algorithm can be trained, we examine a family of 25 naphthalene derivatives. The simplest application of the energy gap law is found to be inadequate to explain the rates of internal conversion (IC) or intersystem crossing (ISC) – the electronic properties of at least one higher-lying electronic state (S_n or T_n) or one far-from-equilibrium geometry are typically needed to obtain accurate results. Indeed, the key descriptors turn out to be the transition state between the Franck–Condon minimum and a distorted local minimum near an S_0/S_1 conical intersection (which governs IC) and the magnitude of the spin–orbit coupling (which governs ISC). The resulting Φ_{fl}'s are predicted with reasonable accuracy ($\pm$ 22%), making our approach a promising ingredient for high-throughput screening and rational design of the molecular excited states with desired Φ's. We thus conclude that our model, while semi-empirical in nature, does in fact extract sound physical insight into the challenge of describing non-radiative relaxations.

Introduction

The rational design of photophysically and photochemically functional materials requires an understanding of their electronic properties.[1–3] For example, the efficiency of many organic electronic devices depends directly on its fluorescence quantum yield (Φ_{fl}), defined by the competition between the fluorescence rate (k_{fl}) and the non-radiative rate (k_{nr}):

$$\Phi_{\mathrm{fl}} = \frac{k_{\mathrm{fl}}}{k_{\mathrm{fl}} + k_{\mathrm{nr}}}. \tag{1}$$

The most obvious example of a photophysical technology where Φ_{fl} is important is an organic light-emitting diode (OLED), in which the total emission efficiency is directly proportional to Φ_{fl}: if an exciton formed in the device undergoes rapid non-radiative decay, no photon is emitted.[4] Similarly, for an organic solar cell (OSC) k_{fl} and k_{nr} determine the exciton lifetime and thereby the probability that an exciton generates charge carriers.[5] These k_{nr}'s are important in many other fields, including: phosphorescent OLEDs,[6–8] biomedical labeling,[9–11] photodynamic therapy,[12–14] laser dyes,[15–17] and luminescent solar concentrators.[18–20]

In reality, the prediction of quantum yields (Φ) has been very difficult. A complete understanding of Φ requires a deep understanding of all the relevant non-radiative decay channels. As these decay channels are, by definition, not emissive, they are difficult to study spectroscopically. For a conventional closed-shell organic molecule, common decay pathways to consider include: internal conversion (IC, $S_1 \rightarrow S_0$), intersystem crossing (ISC, $S_1 \rightarrow T_n$), electron removal and addition ($S_1 \rightarrow D^+$, $S_1 \rightarrow A^-$), and photochemical isomerization ($S_1 \rightarrow S_0^*$).[21] It is challenging to address all of these pathways simultaneously, so we narrow the scope in the present study and focus on the most common decay channels in organic compounds – IC and ISC.

Historically, discussion of IC and ISC has been dominated by the energy gap law.[22–24] When the donating state (S_1) and the accepting state (S_0, T_n) are sufficiently well-separated, the Franck–Condon (FC) factor mediating the transfer decay exponentially with the energy

gap between the two levels.[22–24] The energy gap law thus predicts that the logarithm of the IC rate (k_{IC}) is proportional to the fluorescence energy (E_{fl}):

$$k_{\mathrm{IC}} = A \exp\left(-\frac{E_{\mathrm{fl}}}{k_{\mathrm{B}}T}\right). \tag{2}$$

Eq. (2) is widely used in experimental studies.[24–29]

In the past few decades, the energy gap law has been found to be insufficient.[30] Most crucially, the energy gap law and the very idea of Born–Oppenheimer approximation fail at conical intersections (CI), regions in the phase space where electronic potential energy surfaces (PES) meet one another and the interstate coupling becomes infinite. CIs have been found to be ubiquitous in a variety of chemical systems, including biomolecules where the CIs are believed to help protect from the photodamage. At these CIs a coherent transfer can occur on a sub-picosecond timescale, dominating the overall k_{IC}.[31–42]

Computational studies examining IC pathways involving CIs have become more prevalent in the last decade. Unfortunately, IC is a challenging process to model because it arises from non-adiabatic nuclear dynamics.[32,36,37,40,42–47] Earlier studies have proposed two broad categories of approaches to solve the non-adiabaticity problem. The first approach is to explicitly account for nuclear motions with approximate solutions to the electronic structure.[43–45] The most common way to do this is to run a swarm of trajectories on a real electronic PES. However, converging these trajectories can be very expensive, necessitating a large number of trajectories, and thus limiting the throughput of the approach.[36,37,40] The second approach constructs a static PES from several key molecular geometries of the system in question (usually the global/local minimum and the minimum energy conical intersections (MECI) on the CI seam).[32,42,47] The location of a CI is highly sensitive to the quality of the electronic wave function in use, so the cost of the electronic structure method often limits the size of molecule that can be studied here.

Studies of ISC have also advanced substantially in the past decade.[46,48–55] Although ISC

usually dominates the non-radiative dynamics for small molecules (*e.g.*, the triplet quantum yield in naphthalene, $\Phi_{\mathrm{T}} \approxeq 0.75$[56]), it is a spin-forbidden process that is usually thought not to be responsible for a rapid non-radiative decay, although there are recent counterexamples like 1-nitronaphthalene for which the timescale $\tau_{\mathrm{ISC}} \sim 100$ fs.[48] Compared to IC, ISC is easier to model empirically because it is mediated by spin–orbit coupling (SOC), which can typically be treated perturbatively for organic chromophores. If one works with the spin-diabatic states under the Condon approximation (in which the coupling is independent of nuclear positions), ISC follows a simple rate equation:[57]

$$k_{\mathrm{ISC}} = \frac{2\pi}{\hbar}|H_{\mathrm{SOC}}|^2 \rho(E_{\mathrm{i}} - E_{\mathrm{f}}). \tag{3}$$

The evaluation of $\rho(E_{\mathrm{i}} - E_{\mathrm{f}})$ can still be challenging – the number of FC factors increases dramatically with the number of normal modes.[46] In addition, to quantitatively evaluate k_{ISC} it is sometimes necessary to go beyond the simple Condon approximation, resulting in a truly *ab initio* calculation being computationally infeasible.[50]

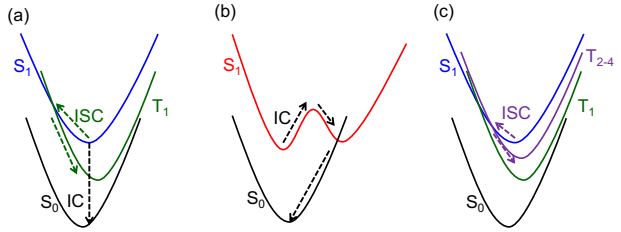


Figure 1: ISC and IC processes investigated in the present study. (a) Direct IC and ISC in which the final states are S_0 and T_1 respectively. (b) Indirect IC that allows a conformational change of S_1 prior to the decay. (c) Indirect ISC in which the final state is a high-lying triplet excited state (T_{2-4}).

In the present work we aim to develop a method to understand and predict Φ_{fl}'s for popular molecular chromophores using only simple and easily accessible information from inexpensive DFT calculations. As should be clear from the discussion above, the DFT calculations themselves do not directly predict Φ_{fl} – they are missing key dynamical information required for a first-principles prediction. The key realization, then, is that there is a

large body of molecules for which Φ_{fl}'s are known experimentally. One can thus use machine learning that is trained on the experimental data to correct for the missing dynamical effects.

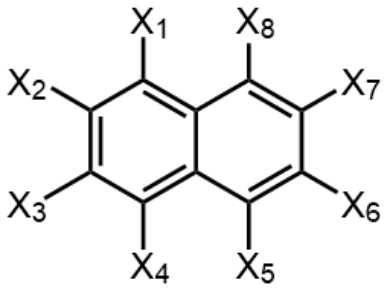
As an illustration, in the present study we show how this approach works for the case of a set of naphthalene derivatives. We show how easily computed quantities such as energy gaps, minimum energy conical intersections (MECI), and SOC, can be combined in order to yield quantitative predictions of Φ_{fl}'s. We discover that, in most cases, information about higher-lying excited states (S_n and T_n) are required to obtain any reasonable description of Φ_{fl}. For example, the 1-aminonaphthalene species are dominated by IC mediated by a transition to a conformation with the amino group distorted out of plane (Fig. 1(b)), which is essentially an $S_1 \rightarrow S_0^*$ isomerization in the adiabatic framework. On the other hand, the alkyl and aryl-substituted naphthalene species are dominated by ISC between S_1 and high-lying triplet states T_{2-4} (Fig. 1(c)). Based on our discovery, the simple energy gap law and direct IC and ISC processes (Fig. 1(a)) are not sufficient to explain the variations in either k_{IC} or k_{ISC}. Using our semi-empirical model, we can reproduce k_{fl}, k_{IC}, and k_{ISC} with mean absolute errors (MAE) of 0.38, 0.68, and 0.34 decades, respectively, and can predict Φ_{fl} with a MAE of 0.22 and a mean signed error (MSE) of 0.10. This study shows how one can understand these ubiquitous decay processes using inexpensive quantum chemical theory.

Theory

Test Molecules

In the present study, we focus on the photophysical processes which occur within two sub-families of naphthalene species (Fig. 2): alkyl- and aryl-substituted naphthalenes (Family I) and 1-aminonaphthalene derivatives (Family II). These families were chosen because of the large quantity of high-quality spectroscopic data that exists in literature to calibrate with, which is very important as the method we outline herein is semi-empirical. The experimental data for Family I were obtained from Berlman *et al.*[58] and those for Family II from the studies

performed by Rückert *et al.*,[59] Suzuki *et al.*,[60] and Takehira *et al.*[61]



Family	#	Name	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
I[58]	**1**	NAPH	H	H	H	H	H	H	H	H
	2	1MN	CH_3	H	H	H	H	H	H	H
	3	2MN	H	CH_3	H	H	H	H	H	H
	4	1HN	OH	H	H	H	H	H	H	H
	5	2HN	H	OH	H	H	H	H	H	H
	6	23DMN	H	CH_3	CH_3	H	H	H	H	H
	7	26DMN	H	CH_3	H	H	H	CH_3	H	H
	8	2PN	H	C_6H_5	H	H	H	H	H	H
	9	14DPN	C_6H_5	H	H	C_6H_5	H	H	H	H
	10	15DPN	C_6H_5	H	H	H	C_6H_5	H	H	H
	11	17DPN	C_6H_5	H	H	H	H	H	C_6H_5	H
	12	ACN	C_2H_4–X_8	H	H	H	H	H	H	C_2H_4–X_1
II[59–61]	**13**	1AN	NH_2	H	H	H	H	H	H	H
	14	1A4CNN	NH_2	H	H	CN	H	H	H	H
	15	1A4CLN	NH_2	H	H	Cl	H	H	H	H
	16	1A4MN	NH_2	H	H	CH_3	H	H	H	H
	17	1MAN	$NHCH_3$	H	H	H	H	H	H	H
	18	1DMAN	$N(CH_3)_2$	H	H	H	H	H	H	H
	19	1DMA4CNN	$N(CH_3)_2$	H	H	CN	H	H	H	H
	20	1DMA4CLN	$N(CH_3)_2$	H	H	Cl	H	H	H	H
	21	1DMA4MN	$N(CH_3)_2$	H	H	CH_3	H	H	H	H
	22	1DMA4MON	$N(CH_3)_2$	H	H	OCH_3	H	H	H	H
	23	1DMA5MON	$N(CH_3)_2$	H	H	H	OCH_3	H	H	H
	24	1DMA6MON	$N(CH_3)_2$	H	H	H	H	OCH_3	H	H
	25	1DMA7MON	$N(CH_3)_2$	H	H	H	H	H	OCH_3	H
	26	1NAZN	*N*-azetidinyl	H	H	H	H	H	H	H
	27	1NPYN	*N*-pyrrolidinyl	H	H	H	H	H	H	H

Figure 2: Test molecules grouped by appropriate families based on their substituents. Family I (# 1–12) includes alkyl- and aryl-substituted naphthalene species and Family II (# 13–27) consists of 1-aminonaphthalene derivatives.

Fluorescence Rate

We evaluated k_{fl} using Einstein's formula for spontaneous emission:[62]

$$k_{\mathrm{fl}} = \frac{4\alpha^3 E_{\mathrm{fl}}^3 |\mu_{\mathrm{fl}}|^2}{3} \tag{4}$$

where $\alpha \simeq 1/137$ represents the fine structure constant, μ_{fl} is the fluorescence transition dipole moment (TDM) between S_1 and S_0. Both E_{fl} and μ_{fl} were calculated using the standard linear-response time-dependent density functional theory (TDDFT) with the Tamm–Dancoff approximation (TDA),[63] at the emissive geometry of S_1 which was also optimized using TDDFT. TDA was chosen because of our empirical observation that singlet–triplet instability tends to be common near the MECIs in the excited state, contaminating full TDDFT results. Thus the TDA results, while less rigorous, are more reliable for the quantities we are computing below.

To simplify our investigation we followed Kasha's rule in the present study – all molecules emit from their lowest-energy excited state of a given multiplicity.[64,65] This means that E_{fl} and μ_{fl} become E_{S_1} and μ_{S_1}. To help benchmark our methodology, we also calculated the absorption energy, E_{abs}, based on TDDFT, at the S_0 geometry (optimized using ground state DFT).

Internal Conversion Rate and Conical Intersection

We described k_{IC} following an Arrhenius-like ansatz modified from Eq. (2),

$$k_{\mathrm{IC}} = A_{\mathrm{IC}} \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T}\right). \tag{5}$$

The determinations of the activation energy (E_{a}), and the pre-exponential factor (A_{IC}) were the main tasks of this part of the study.

An earlier CASPT2 study on 1-aminonaphthalene (compound **13**) by Montero *et al.*

showed that CIs play a key role in the photophysics.[66] The complete characterization of a CI between two states is difficult as the CI is in actuality a multi-dimensional hyper-seam.[41] The MECI on this seam is one effective way to describe a CI. To locate the MECI between two PES's, we used the penalty-function method proposed by Levine *et al.*[67] and implemented by Zhang *et al.*[68] (selecting $\gamma = 0.02$ Hartree).

Our principal tool, the standard linear-response TDDFT, does not properly describe a CI as it gives the CI seam an incorrect dimensionality.[69] However, the spin-flip variant of TDDFT (SFDFT)[70] does not have the dimensionality problem and is a useful tool for finding the MECI between S_1 and S_0 as a rough approximation of the S_1/S_0 CI. However, SFDFT necessitates the use of an exotic functional with unusually a large amount of Hartree–Fock (HF) exchange to be accurate:[70–73] we here employed the common BHHLYP (with 50% HF and 50% Becke exchange[74] and the Lee–Yang–Parr correlation[75]).

To anchor our results in the more-familiar linear-response TDDFT approach, we constructed a reaction path from the FC minimum of S_1 state to the SFDFT-evaluated MECI geometry using standard linear-response TDDFT and the freezing string method (FSM),[76,77] and located the transition state near the maximum of this reaction path. E_a in Eq. (5) was calculated as the energy difference between the FC minimum of S_1 and the transition state, and A_IC was obtained from a linear fit between the computed E_a and the experimental $\log_{10} k_\mathrm{IC}$.

Intersystem Crossing Rate and Spin–Orbit Coupling

We described k_ISC following a modified version of Eq. (3),

$$k_\mathrm{ISC} = B_\mathrm{ISC} + C_\mathrm{ISC} \sum_i |H_\mathrm{SOC}^{\mathrm{S_1/T}_i}|^2, \tag{6}$$

in which $H_\mathrm{SOC}^{\mathrm{S_1/T_i}}$ represents the SOC between S_1 and energetically-local triplets (T_i) and B_ISC and C_ISC are parameters whose values are trained to experimental data below.

Recent work by Marian and coworkers[78] has expanded the calculation of $H_{\mathrm{SOC}}^{\mathrm{S_1/T}_i}$ within the framework of TDDFT. Herein we employed the one-electron Breit–Pauli Hamiltonian,[79]

$$H_{\mathrm{SOC}} = -\frac{\alpha^2}{2} \sum_{k,A} \frac{Z_A}{r_{kA}^3} (\mathbf{r}_{kA} \times \mathbf{p}_k) \cdot \mathbf{s}_k, \tag{7}$$

and evaluated $H_{\mathrm{SOC}}^{\mathrm{S_1/T}_{i=2-4}}$ at the TDDFT-optimized S_1 geometry. In Eq. (7) k and A index electrons and nuclei, Z_A is the charge of nucleus A, $\mathbf{p}_k$ and $\mathbf{s}_k$ are the momentum and spin vectors of electron k respectively, and $\mathbf{r}_{kA}$ represents the displacement vector from nucleus A to electron k. B_{ISC} and C_{ISC} were obtained from the linear fit of the relation between the computed $|H_{\mathrm{SOC}}^{\mathrm{S_1/T}_i}|^2$ and the experimental k_{ISC}.

Quantum Yield

In the present study, we computed Φ_{fl} following Eq. (1) and employed[80]

$$k_{\mathrm{nr}} \simeq k_x \quad (x = \mathrm{IC} \quad \mathrm{or} \quad \mathrm{ISC}). \tag{8}$$

Eq. (8) expresses the assumption that one of the two decay processes, either IC or ISC, is considered dominant (more than one order of magnitude greater than any other non-radiative decay process). Although we chose the dominant pathway based on experimental evidence, we believed that extending our methodology to be fully black-box is viable. In particular, when focusing on only one decay process or the other, we found that simple regression is effective at predicting k_{nr}'s. For a general case, we anticipated that an artificial neural network[81–83] would easily be able to decide which pathway is more likely to dominate and choose the appropriate descriptor.

Computational Details

All DFT calculations were performed in Q-Chem 4.4[84] using the ωB97X-D3 functional[85] and the 6-31G* basis set,[86] except when explicitly noted. ωB97X-D3 was used because most popular XC functionals like B3LYP struggle to reproduce the S_1/S_2 (L_b/L_a) ordering in polycyclic aromatic hydrocarbons like naphthalene derivatives.[87,88] For example, for plain naphthalene (compound **1**) B3LYP inverts the S_1/S_2 gap ($E(S_2) - E(S_1) = -0.09$ eV) compared to the experimental value (0.53 eV), while ωB97X-D3 predicts the correct ordering with a gap of 0.32 eV.

Results and Discussion

Fluorescence Energies and Rates

To compute Φ_{fl} of a given molecule we first need an accurate emissive geometry. We employed standard TDDFT/TDA to acquire S_1 geometries and reproduced E_{fl}'s with a MAE of 0.71 eV, as shown in Fig. 3(a). The MAE of E_{abs}'s is 0.66 eV, with results presented in Fig. S1 of the Supporting Information (SI). Both results appear quite poor for TDDFT, for which the typical intrinsic MAE is $\sim$0.3 eV. Fig. 3(a) illustrates that this large MAE arises from a uniform overestimation of the predicted E_{fl}'s. Simply calibrating our results by treating 0.71 eV as a systematic error and subtracting it from all E_{fl}'s produced an improved MAE of 0.06 eV, reflecting that our results are qualitatively very accurate.

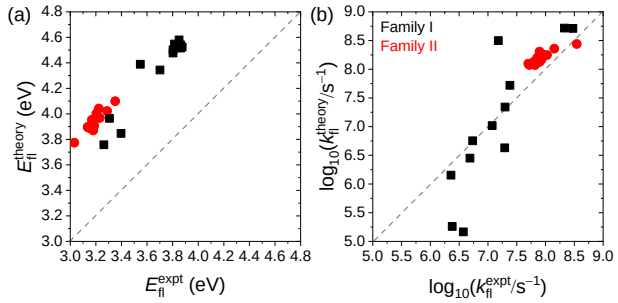


Figure 3: Comparison between the theoretical and experimental values for (a) E_{fl}'s and (b) k_{fl}'s for Kasha emissions ($S_1 \rightarrow S_0$). The dashed lines show perfect predictions. Molecules in Families I and II are represented by black squares and red circles, respectively.

Having obtained satisfactory emissive geometries, we compared calculated k_{fl}'s against the experiments based on Eq. (4) and presented the results in Fig. 3(b). While past studies reported that the TDDFT evaluation of μ_{fl} is difficult,[87,88] we found the calculated μ_{fl}'s acceptable, reproducing k_{fl}'s with a MAE of 0.38 decades. Much of the error arises from large underestimations of k_{fl}'s of the poorly emissive compounds naphthalene (**1**) and 1-methylnaphthalene (**2**), possibly reflecting the limitation of the "frozen" Condon approximation.

Direct Intersystem Crossing and Internal Conversion Transitions

As discussed in the introduction, conventional models of IC and ISC are often limited to a direct transfer from S_1 to S_0 and T_1, respectively. Under the energy gap law assumption (*e.g.* Eq. (2)), $\log_{10}k_{\mathrm{nr}}$ should be linearly anticorrelated with the energy gap. To evaluate the quality of such an energy gap law relation, we started with direct IC and checked the predictive utility of E_{fl} and the reorganization energy of direct IC (λ_{IC}, Fig. 1(a)), which is defined in Marcus theory[89] and coincides with half of the Stokes shift ($E\mathrm{ss} = E_{\mathrm{abs}} - E_{\mathrm{fl}}$).[90] Fig. 4 (a) and (b) illustrates the reported experimental k_{nr} as a function of the experimental E_{fl} and λ_{IC}. Here we used experimental photophysical observables as the independent variables in order to show that the problem does not lie in the quality of electronic structure theory, but in the energy gap law model itself. As one can see, both

correlations are poor.

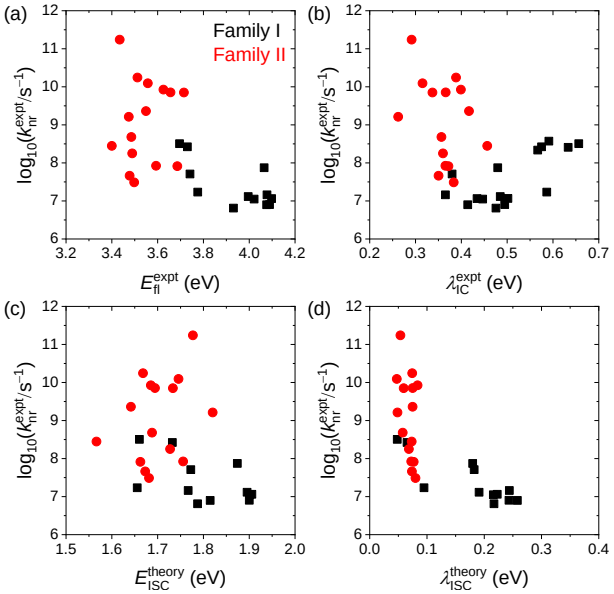


Figure 4: Energy gap law correlations between the experimental $\log_{10}k_{\rm nr}$ and the experimental (a) $E_{\rm fl}$ and (b) $\lambda_{\rm IC}$ for the direct $S_1 \rightarrow S_0$ IC, and between the experimental $\log_{10}k_{\rm nr}$ and the computed adiabatic (c) $E_{\rm ISC}$ and (d) $\lambda_{\rm ISC}$ for the direct $S_1 \rightarrow T_1$ ISC. Molecules in Families I and II are presented by black squares and red circles, respectively.

We performed a similar analysis for direct ISC (Fig. 1(a)), using the computed adiabatic energy gap ($E_{\rm ISC}$) and reorganization energy ($\lambda_{\rm ISC}$) and plotting their correlations with the experimental $\log_{10}k_{\rm nr}$ in Fig. 4 (c) and (d). These results indicate an analogous difficulty predicting $k_{\rm ISC}$ using simply the energy gap law. Overall, our results support the conclusion that the energetics of S_1 and T_1 are generally insufficient to predict $k_{\rm nr}$'s on their own. As we will see below, $\Phi_{\rm fl}$ typically has a critical dependence on higher-lying electronic states or far-from-equilibrium geometries, which must be accounted for if one expects accurate predictions.

Intersystem Crossing

We found that $k_{\rm ISC}$'s for the alkyl- and aryl-substituted naphthalene compounds (Family I)[58] are best modeled by Eq. (6) where the accepting triplet states are the energetically accessible states that are *not* the lowest triplet state. The absence of T_1 is perhaps obvious based

on El Sayed's rule, which dictates that the SOC between S_1 and T_1 is typically negligible because the two states have the same orbital character. This equation uses a "frozen" Condon approximation,[57] with the additional assumption that all relevant accepting states (T_2, T_3, and T_4) have equal accepting densities of states at the energy of the donating S_1 state. Herein we plot the experimental $\log_{10}k_{\rm nr}$ versus the computed total $\log_{10}k_{\rm ISC}$ in Fig. 5, showing a reproduction of the experimental $k_{\rm nr}$'s with a MAE of 0.34 decades, which is extremely good. We also experimented with other relations that incorporate energetic dependence into an Arrhenius-like or Marcus-like expression, but at least for this case there is no correlation between the TDDFT energies and $k_{\rm ISC}$'s. The difficulty might originate in the very small S_1/S_2 gap for Family I, which challenges the accuracy of our excited-state methodology.

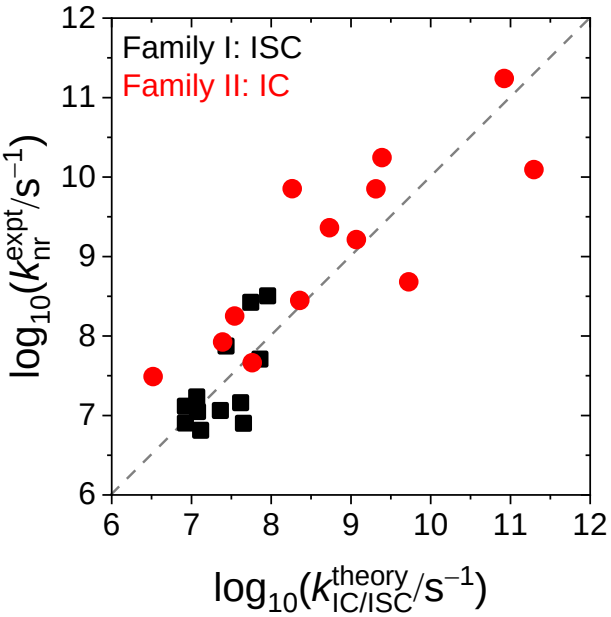


Figure 5: Comparison between the computed $k_{\rm ISC}$ (Family I, black squares) or $k_{\rm IC}$ (Family II, red circles) and the experimental $k_{\rm nr}$ on the logarithm scale. Family I are dominated by IC while Family II are dominated by ISC.

Internal Conversion

One of the advantages of the 1-aminonaphthalene data set (Family II) is the availability of experimental $E_{\rm a}$'s of IC (Eq. (5)). Fig. 6 shows the experimental $\log_{10}k_{\rm nr}$ versus the

experimental E_a. The results are compared to the TDDFT-evaluated E_a required to reach the transition state from the FC minimum along a reaction path similar to the one shown in Fig. 7.

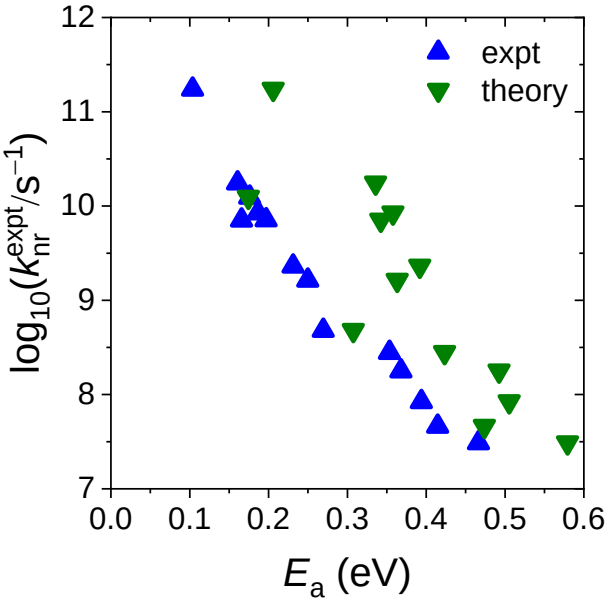


Figure 6: Energy gap law correlations between the experimental $\log_{10}k_{nr}$ and the experimental (blue up triangles) or TDDFT-evaluated (green down triangles) E_a for 1-aminonaphthalene derivatives (Family II).

We observed that the experimental E_a is a very good predictor of the experimental k_{nr} through the modified energy gap law (similar to Eq. (5)) – the prefactor A varies very little.[1] The near-constant value of A essentially validates the idea that this family of chromophores is chemically similar. For a more diverse set of molecules, one expects that both A and E_a would vary significantly. As shown in Fig. 6, although TDDFT slightly overestimates the experimental E_a's it captures the variation of A very well. A simple linear fit of the $\log_{10}k_{nr}$ to the TDDFT-computed E_a allows us to reproduce k_{nr} accurately with a MAE of 0.68 decades (Fig. 5), which is in a fairly good agreement given that these k_{nr}'s vary over four decades. Figs. 5 and 6 show that these E_a's predict k_{IC}'s very accurately – we have now constructed an adequate method for computing the total k_{nr}'s of 1-aminonaphthalenes

[1]Note that for 1DMA7MON, no experimental activation energy was reported, so it is omitted from the plot.

derivatives. In addition, we can use the SFDFT[70] approach and the BHHLYP functional[74,75] to evaluate the S_1/S_0 MECI, and directly construct a Bell–Evans–Polanyi model[91,92] using the theoretical energy gap between the S_1 FC minimum and this MECI. The result, presented in Fig. S2 of the SI, reproduces k_{IC} with a MAE of 0.27 decades.

Above, we showed that IC occurring in Family II cannot be understood as a one-step, direct $S_1 \rightarrow S_0$ transition from the vicinity of the emissive geometry. It is thus interesting to evaluate the nature of the transition state involved. The computed reaction path for 1-aminonaphthalene (**13**) is shown in Fig. 7, highlighting the distorted molecular configurations of the MECI and the transition state near it. The resulting structure is characteristic of all members of Family I: IC is mediated by a transition from the FC minimum to a novel conformer with the amino group and the C_1 atom (Fig. 2) bonded to it dragged nearly perpendicular to the naphthalene plane. When stretched in this manner, the transition density is localized to the amino group and the C_1 and C_2 atoms (Fig. 7).

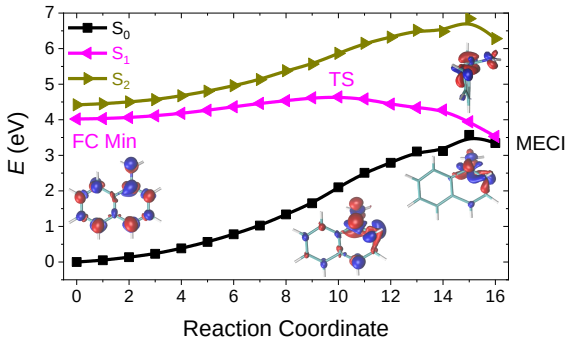


Figure 7: PES's are plotted along the IC reaction coordinate for the S_0 (black squares), S_1 (magenta left triangles), and S_2 (dark yellow right triangles) states of 1-aminonapthalene (compound **13**). From left to right, we present molecular geometries and transition densities for the S_1 PES at the FC minimum, the transition state, and at the S_0/S_1 MECI (side and front views).

This conformational isomerization mechanism ($S_1 \rightarrow S_0^*$) rationalizes trends observed in the experimental measurements of **13**. For a given amino substitution, a roughly inverse energy gap law relation is observed: as E_{fl} decreases, k_{IC} also decreases. This trend, which has also been observed elsewhere,[93] is contrary to the conventional wisdom, but can be easily understood in our framework. If the IC process is simply limited by the activation

of a transition state, under a Bell–Evans–Polanyi model we would predict that the relative energies of the two minima provide E_a.[91,92] Assuming identical energies of the near-CI region for all species with the same amino substitution (justified by the spatial localization of the excitation near the amino group), E_a is determined only by the energy of the near-FC region, which is conveniently probed by E_{fl} . A larger E_{fl} indicates a more downhill IC mechanism, implying a more energetically accessible transition state and thus a faster IC process, in opposition to the traditional energy gap model.

The nature of the IC pathway for compounds in Family II has been investigated in several past studies.[59–61] Most notably, Montero *et al.*[66] performed CASPT2 calculations and concluded that IC decay proceeded via an S_1/S_2 CI followed by transfer through an S_2/S_0 CI. However, experimentally they found no evidence for a relevant S_1/S_2 CI in the photodynamics. Our results do not necessarily rule out the presence of an S_1/S_2 CI or its relevance to IC in these derivatives. However, our comparison over a broad family of derivatives shows that any relevant information about the S_1/S_2 CI must be encoded in the transition state – either because going over the transition state is the rate-determining step or because the electronic structures of S_1 and S_2 are substantially mixed at the transition state. This kind of insight cannot be obtained from a case study on a single derivative.

Quantum Yield Evaluation

With all of the results obtained above, we can finally evaluate our ability to compute Φ_{fl} using Eq. (1). We illustrate in Fig. 8 the correlation between our computed Φ_{fl}'s and the experimental values, achieving a MAE of 0.22 and a MSE of 0.10.

We visually note that these plots illustrate one of the challenges in the estimation of Φ_{fl}: while the predicted k_{fl}'s and k_{nr}'s are obviously quite good, the resulting Φ_{fl}'s are less inspiring. The reason for this is the non-linear nature of Φ_{fl}: cases with very fast (slow) k_{nr}'s are squeezed together near $\Phi_{fl} \approx 0$ ($\Phi_{fl} \approx 1$), leading to a high sensitivity to errors over a small range of k_{nr}'s.

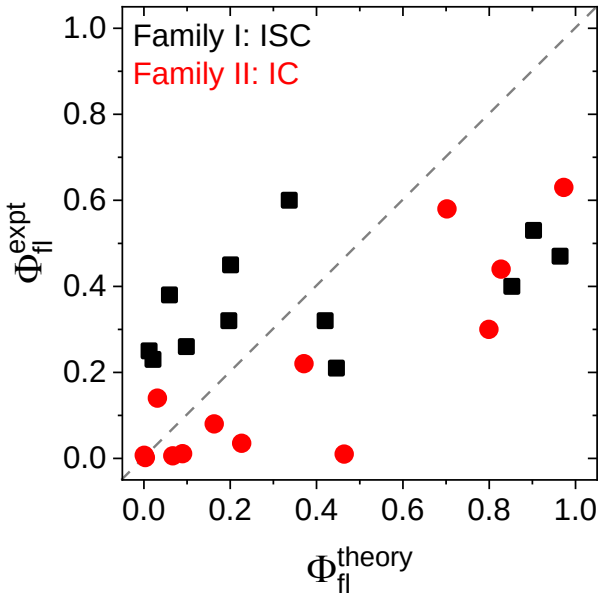


Figure 8: Comparison between computed and the experimental Φ_{fl}'s. Family I are dominated by IC while Family II are dominated by ISC.

We therefore analyzed which predicted components, k_{fl} or k_{nr}, limit the accuracy of Φ_{fl} most by replacing either computed k_{fl} or k_{nr} with its experimental counterpart in Eq. (1). If we combined the computed k_{fl}'s with the experimental k_{nr}'s, we obtained Φ_{fl}'s with a MAE of 0.12, which is comparable to the experimental error.[58] Similarly, when we combined the computed k_{IC}'s of Family II with the experimental k_{fl}'s we arrived at a MAE of 0.12 which, again, is very accurate. However, combining the computed k_{ISC}'s of Family I with the experimental k_{fl}'s produces a MAE of 0.16, slightly worse than the other results. This result suggests that the greatest room for improvement lies in k_{ISC}'s, which is unsurprising considering the crudeness of our approximations.

Conclusions and Future Work

In the present work, we analyzed the components necessary for the calculation of Φ_{fl}, determined from competition between k_{fl} and the relevant k_{nr} for the system. When combined with appropriate training on experimentally known values of Φ_{fl}, we found that TDDFT is

an adequate tool to compute the absolute k_{fl}, yielding a MAE of 0.38 decades. In particular, our results call into question any attempts to predict Φ's based on near-equilibrium energetics of the lowest-lying excited states (S_1 and T_1). In all cases, we discovered that far-from-equilibrium conformations and/or higher-lying excited states play a central role in accurately predicting Φ_{fl}. In particular, heuristics such as the energy gap law seem to provide unreliable conclusions.

Herein, we provided more reliable predictions of k_{nr}'s by constructing and using a semi-empirical model for the specific case of napthalene derivatives. For IC-dominated species we introduced an Arrhenius-like scheme using the TDDFT-evaluated E_{a} for the transition from the FC minimum of the S_1 PES to a novel, amino-distorted transition-state conformer reproducing k_{IC}'s with a MAE of 0.68 decades. For ISC-dominated ones we applied a "frozen" Condon approximation in which T_2, T_3, and T_4 are all equally accessible, resulting in k_{ISC}'s with a MAE of 0.34 decades. Combining these results, we obtained Φ_{fl}'s with a MAE of 0.22 and a MSE of 0.10.

While the details of the approximations here are not universally applicable (including the frozen Condon approximation and the neglect of the $S_0 \rightarrow S_2$ excitation), we expect that moving forward this study can provide a blueprint for predicting the Φ_{fl}'s of other families of fluorescent dyes. Such studies provide the tantalizing possibility of high-throughput screening of photoactive molecules based on Φ's: one defines a family of molecules, trains the predictions on a small, representative set of chromophores from that family using supervised machine learning, and then uses inexpensive computational schemes to screen for potential high-Φ_{fl} or low-Φ_{fl} molecules (depending on the demand) within the nearby chemical space that can be synthesized. As the first step in this direction, we anticipate future work on families of molecules for which understanding the photophysical decay pathways are more chemically significant, such as the boron-dipyrromethene (BODIPY) derivatives. More work into understanding ISC pathways in general is also merited, as our understanding evinced here can be improved.

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Graphical TOC Entry