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First-principles calculations of anharmonic and deuteration effects on photophysical properties of polyacenes and porphyrinoids

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Abstract

A new method for calculating internal conversion rate constants (k_{IC}), including anharmonic effects and using the Lagrangian multiplier technique, is proposed. The deuteration effect on k_{IC} was investigated for naphthalene, anthracene, free-base porphine (H₂P) and tetraphenylporphyrin (H₂TPP). The results show that anharmonic effects are important when calculating k_{IC} for transitions between electronic states that are energetically separated (ΔE) by more than 20000-25000 cm⁻¹. Anharmonic effects are also important when $\Delta E < 20000-25000$ cm⁻¹ and when the accepting modes are X-H stretching vibrations with a frequency larger than 2000 cm⁻¹. The calculations show that there is a mixture between the S₁ and S₂ states of naphthalene induced by non-adiabatic interactions. The non-adiabatic interaction matrix element between the S₁ and S₂ states is 250 cm⁻¹ and 50 cm⁻¹ for the normal and fully deuterated naphthalene structure and this difference significantly affects the estimated fluorescence quantum yield. Besides aromatic hydrocarbons, (H₂P) and (H₂TPP), the k_{IC} rate constant is also calculated for pyrometene (PM567) and tetraoxa[8]circulene (4B) with a detailed analysis of the effect of the vibrational anharmonicity.

1. Introduction

Accurate and detailed information about molecular photophysical properties is necessary in many applications like development of optical devices and organic light emitting diodes (OLEDs) [1-3], dye-based lasers [4-6], upconverting nanoparticles [7-9], bioimaging and photodynamic therapy devices [10-12]. Molecular photophysical properties are also very important for elucidating chemical processes in the lower atmosphere and interstellar clouds, like photolysis of molecules in gases [13-15], smog and aerosol particle formation [16, 17]. The key parameters of photophysical properties are the rate constants for radiative and non-radiative transitions [18-21]. Knowledge about them gives the opportunity to estimate the quantum yield of photophysical and photochemical processes. For example, the fluorescence quantum yield (ϕ_f) can be estimated using the simple formula $\phi_f = k_r / (k_{nr} + k_r)$, where k_r is the rate constant of the radiative transition and k_{nr} is the total rate constant of the non-radiative transitions between initial and final electronic states [21]. At low molecular concentrations when the intermolecular interactions are very weak, a simple expression holds: $k_{nr} = k_{IC} + k_{ISC}$, where k_{IC} is internal conversion (IC) rate constant between electronic states with the same spin multiplicity and k_{ISC} is the intersystem crossing (ISC) rate constant between electronic states with different spin multiplicities [21]. The k_{IC} and k_{ISC} rate constants can be calculated using various softwares at different levels of theory [19, 20, 22-27]. The most popular method is based on correlation functions for estimating Franck-Condon contributions [22-25]. The problem of the summation of final states is then converted into time-domain integration using Fourier transformation. Another approach for calculating k_{IC} and k_{ISC} is to explicitly consider final states with selected accepting modes [20, 26-29]. Calculating the k_{ISC} constant is generally not a very difficult task. The k_{ISC} value can even be estimated using the Marcus's theory [30, 31]. However, calculating k_{IC} is more difficult, since the non-adiabatic coupling interaction matrix element (NACME) between the electronic states of the same spin multiplicity is needed.

Moreover, large energy gaps between the two lowest singlet states (S_1 and S_0) are challenging for IC theory, because anharmonic effects may be significant [21].

Recently, we have developed a first principle method for calculating k_{IC} and k_{ISC} , which has been successfully applied to a number of organic and organometallic molecules for which the experimental data were available [27, 32]. We obtained rate constants in a good agreement with experimental data when the Franck-Condon and the adiabatic approximations hold. Some exceptions were found for polyacenes and free-base porphyrin (H_2P) [27]. H_2P is a rigid molecule possessing a very small Stokes shift ($<100\text{ cm}^{-1}$), which implies that the Huang-Rhys factors are small [27]. We suggested that the non-adiabatic interaction induced mixing between the first (S_1) and second (S_2) excited singlet electronic states is the main reason for the deviation of the calculated rate constants from the experimental ones. We recently extended our approach by additionally accounting for Herzberg-Teller effects using fitting curves [26]. The extended method was successfully used in calculations of photophysical properties of H_2P , showing that the k_{IC} rate constant of H_2P can be accurately estimated in the Herzberg-Teller approximation. In our recent studies, we considered molecules that fluoresce with energies below 25000 cm^{-1} [26, 27]. The calculations showed that k_{IC} is small when the energy difference between S_1 and S_0 is larger than 20000 cm^{-1} , implying that the IC rate is much slower than the ISC rate and the rate of radiative processes [28]. In the harmonic approximation, k_{IC} decreases rapidly with increasing energy difference when the gap exceeds 25000 cm^{-1} [26, 27]. Large energy gaps imply that molecular vibrations with high quantum numbers and consequently with significant anharmonicity are involved in the non-radiative transition. In calculations of k_{IC} rates, Plotnikov studied anharmonic effects by considering only vibrational modes involving X-H bonds (X=C, O and N atoms), because they have the largest anharmonicities [28]. The problems to estimate k_{IC} for transitions whose energies exceed 25000 cm^{-1} have been discussed by Makshantsev [33, 34]. Accurate k_{IC} rate constants for benzene, naphthalene, anthracene, and other

molecules whose transition energies are larger than 25000 cm^{-1} can be calculated only by considering anharmonic effects [35].

In this work, we have implemented methods to calculate anharmonic effects into our algorithm to calculate rate constants for non-radiative transitions [26, 27]. We have also implemented an algorithm to calculate Franck-Condon factors using the method of Lagrange multipliers [21]. The modified methods are used for calculating k_{IC} for benzene, naphthalene and anthracene for which the anharmonicity plays a crucial role. The method has also been used for calculating k_{IC} for free-base porphyrin (H_2P), free-base tetraphenylporphyrin (H_2TPP), pyrometene (PM567) and tetraoxa[8]circulene (4B) (Figure 1), which emit light in the different areas of the electromagnetic spectrum [26, 27]. We also compare the rate constants and quantum yields with values obtained in previous calculations. Rate constants are calculated for perdeuterated naphthalene, anthracene, H_2P , and H_2TPP (D_2P , and D_2TPP) in order to investigate the influence of the deuteration on their photophysical properties. We have also estimated the non-adiabatic coupling induced mixing between the S_1 and S_2 states of the naphthalene and anthracene species.

Figure 1. The molecular structures of the studied molecules.

2. Theory

2.1. The general formula

Calculations of non-radiative rate constants for transitions between electronic states is difficult due to the many factors that influence the mechanisms of the physical processes. Non-radiative electronic transitions must fulfil many conditions [21]. First of all, they must be irreversible [21], which can occur in the limit of high density of states when the Bixon-Jortner model [29] is applicable or in the intermediate case [21, 28]. The statistic limitation corresponds to a large density of final states. In the polyatomic molecules, the density of final states is large when the energy gap amounts to several eV [21]. However, all final states are not effective or accepting in non-radiative processes. Some states accept energy with high probability in non-radiative processes [21]. The density of states of these so called effective states is important for non-radiative electronic transitions. For small density of states, the non-radiative electronic transitions have resonance character and the broadening of the final states can be described by a Lorentzian function, whose width corresponds to the lifetime of the vibration relaxation [21, 28]. Thus, the irreversibility of non-radiative electronic transitions is due to small lifetimes of the effective states. The intermediate case is more general and the expression of k_{nr} can be expressed as [21, 28]:

$$k_{nr} = \sum_n \left| V_{i0,fn} \right|^2 \Gamma_{fn} \left[\Delta_{if}^2 + \frac{\Gamma_{fn}^2}{4} \right]^{-1} \quad (1),$$

where i is the initial electronic state, f is the final electronic state, n is a vibrational level of the final state, Γ_{fn} is the relaxation width of the vibrational level $|fn\rangle$, $\Delta_{if} = |E_{i0} - E_{fn}|$ is the energy difference between the initial and final vibrational states, and $V_{i0,fn}$ is the matrix element of the perturbation operator. Only the lowest vibrational level of the initial state is considered. Actually, temperature effects can be also accounted for by using Eq. (1). However, in many of the applications discussed in the introduction, it is enough to consider the low-temperature condition of the electronic transitions. The perturbation operator is the spin-orbit

coupling interaction for ISC transitions and the non-adiabatic coupling interaction for IC processes. Eq. (1) written in atomic units holds at ambient temperatures ($T \leq 300$ K) when $k_{nr} \ll \Gamma_{fn}$. When the $k_{nr} \ll \Gamma_{fn}$ condition does not hold, then $k_{nr} \sim 0.5 \cdot \Gamma_{fn}$ applies [28].

In general, the energy of the excited electronic state is transferred into the effective states of the accepting vibrational modes. The energy is then converted into other vibrational modes of molecule or into vibrational modes of the solvent or of other surrounding molecules resulting in irreversibility of the non-radiative electronic transition.

Γ_{fn} depends on the molecular structure and the n value [36, 37]. However, the order of magnitude of k_{nr} is nearly independent of Γ_{fn} when $10^{12} \text{ s}^{-1} < \Gamma_{fn} < 10^{14} \text{ s}^{-1}$ holds [28]. The effect of different spectral line shapes and widths of the final state has recently been investigated [25], where they showed that the broadening profile of the final state is very important. For example, Lorentzian broadening influences strongly the calculated k_{nr} value when using the autocorrelation function approach. Although the choice of the spectral line shape function of the final state is still under debate, the Lorentzian shape function is in general a good choice. Since it is difficult to calculate Γ_{fn} , it is better to estimate its value from experimental data [25]. A typical value for Γ_{fn} is $\sim 10^{14} \text{ s}^{-1}$ [28], which we adopt in this work.

The following approximations have previously been used in our calculations of the rate constants of non-radiative transitions:

- 1) *The harmonic approximation*, where the harmonic oscillator model is used for the initial and final vibrational states.
- 2) *The adiabatic approximation* for the initial and final electronic states is used.

- 3) *The linear coupling model*, where the vibrational frequencies of the initial and final states are the same and the displacement of the equilibrium position is considered only in the calculation of the matrix elements of the Franck-Condon and Herzberg-Teller factors. Here, we introduce the y parameters, which reflect the displacement of the equilibrium position of each harmonic oscillator. The linear coupling model is valid, when the Duschinsky effect is small.
- 4) In the *Herzberg-Teller approximation*, the matrix elements of the perturbation operator are expanded along the normal coordinates. The zeroth-order and first-order terms are considered.

The rate constants in Eq. (1) for the different physical processes can then be written as [26]:

$$k_{ISC-FC} = \frac{4}{\Gamma_f} \left(H_{SO}^{if} |_{\vec{R}=\vec{R}_0} \right)^2 P, P = \sum_{n_1, n_2, \dots, n_{3N-6}}^{E_{if} = n_1 \omega_1 + n_2 \omega_2 + \dots + n_{3N-6} \omega_{3N-6}} \prod_{k=1}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right), \quad (2)$$

$$k_{ISC-HT} = \sum_{j=1} (t_j W_j \sqrt{P_j})^2, P_j = \sum_{n_1, n_2, \dots, n_{3N-6}}^{E_{if} - n_j \omega_j = n_1 \omega_1 + n_2 \omega_2 + \dots + n_{3N-6} \omega_{3N-6}} \prod_{\substack{k=1 \\ k \neq j}}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right), \quad (3)$$

$$k_{IC-FC} = \frac{4}{\Gamma_f} \sum_{j=1} (d_j \cdot b_j \sqrt{P_j})^2, P_j = \sum_{n_1, n_2, \dots, n_{3N-6}}^{E_{if} - n_j \omega_j = n_1 \omega_1 + n_2 \omega_2 + \dots + n_{3N-6} \omega_{3N-6}} \prod_{\substack{k=1 \\ k \neq j}}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right), \quad (4)$$

$$k_{IC-HT} = \frac{4}{\Gamma_f} \sum_j \sum_{j'} (b_j t_{j'} W_{jj'} \sqrt{P_{jj'}})^2, P_{jj'} = \sum_{n_1, n_2, \dots, n_{3N-6}}^{E_{if} - n_j \omega_j - n_{j'} \omega_{j'} = n_1 \omega_1 + n_2 \omega_2 + \dots + n_{3N-6} \omega_{3N-6}} \prod_{\substack{k=1 \\ k \neq j \\ k \neq j'}}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right) \quad (5),$$

where,

$$W_{jj'} = - \sum_v \sum_q \sum_{v'} \sum_{q'} < \frac{\varphi_i(\vec{r}, \vec{s}, \vec{R}) \partial^2 \varphi_f(\vec{r}, \vec{s}, \vec{R})}{\partial R_{vq} \partial R_{v'q'}} > |_{\vec{R}=\vec{R}_0} M_v^{-1/2} M_{v'}^{-1/2} L_{vqj} L_{v'q'j'} \quad (6)$$

$$D = - \sum_v \sum_q (2M_v)^{-1} < \varphi_i(\vec{r}, \vec{s}, \vec{R}) | \frac{\partial^2}{\partial R_{vq}^2} | \varphi_f(\vec{r}, \vec{s}, \vec{R}) > |_{\vec{R}=\vec{R}_0}, \quad (7)$$

$$d_j = - \sum_v \sum_q M_v^{-1/2} L_{vqj} < \varphi_i(\vec{r}, \vec{s}, \vec{R}) \frac{\partial \varphi_f(\vec{r}, \vec{s}, \vec{R})}{\partial R_{vq}} > |_{\vec{R}=\vec{R}_0}, \quad (8)$$

$$t_j = < \chi_{i0_j}(Q_j) | Q_j | \chi_{fn_j}(Q_j) > = \left[\frac{1}{2\omega_j n_j!} (n_j + y_j)^2 \cdot e^{-y_j} \cdot y_j^{n_j-1} \right]^{1/2}, \quad (9)$$

$$b_j = \langle \chi_{i0_j}(Q_j) | \frac{\partial}{\partial Q_j} | \chi_{fn_j}(Q_j) \rangle = \left[\frac{1}{2n_j!} \omega_j (n_j - y_j)^2 \cdot e^{-y_j} \cdot y_j^{n_j-1} \right]^{1/2}, \quad (10)$$

$$y_j = \frac{1}{2} (\omega_j) \cdot |Q^f_{0_j} - Q^i_{0_j}|^2, \quad (11)$$

$$W_j = \left[\sum_v \sum_q \left(\frac{\partial(H_{so}^{if})}{\partial R_{vq}} \right)_{R=\bar{R}_0} M_v^{-1/2} L_{vqj} \right]. \quad (12).$$

Here, $\langle \varphi_i(\bar{r}, \bar{s}, \bar{R}) \frac{\partial \varphi_f(\bar{r}, \bar{s}, \bar{R})}{\partial R_{vq}} \rangle_{\bar{R}=\bar{R}_0}$ and $\langle \frac{\varphi_i(\bar{r}, \bar{s}, \bar{R}) \partial^2 \varphi_f(\bar{r}, \bar{s}, \bar{R})}{\partial R_{vq} \partial R_{v'q'}} \rangle_{\bar{R}=\bar{R}_0}$ are the non-

adiabatic coupling matrix elements (NACMEs) of the first and second order, respectively. M_v is the mass of the v^{th} atom, L_{vqj} are coefficients of the linear relation between the Cartesian (R) and the normal coordinates (Q): $R_{vq} - R_{0vq} = M_v^{-1/2} L_{vqj} Q_j$. The t_j and b_j integrals are the Herzberg-Teller and non-adiabatic factors, respectively. The y_j parameter is the Huang-Rhys factor of the j^{th} accepting mode. H_{so}^{if} is a matrix element of the spin-orbit coupling (SOC) interaction. The E_{if} value is the energy gap between the initial and the final states, and n_j and ω_j are the excitation quantum number and the frequency of the j^{th} vibrational mode, respectively. The P , P_j and $P_{jj'}$ values depend on the energy E_{if} and can easily be estimated using the fitting curves published in the Ref. [26].

2.2. The Lagrange multiplier method for estimating P , P_j and $P_{jj'}$

In this work we estimate P , P_j and $P_{jj'}$ values using Lagrange multipliers. In order to do that, we construct the Lagrange function

$$L = \ln \left[\prod_{k=1}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right) \right] - \lambda \left(\sum_{k=1}^{3N-6} n_k \omega_k - E_{if} \right) \quad (13)$$

The equation system of the Lagrange function leads to an expression for each quantum number when the product $\left[\prod_{k=1}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right) \right]$ reaches a maximum [21]:

$$n_k = y_k \exp(-\omega_k \lambda) \quad (14),$$

where λ is the Lagrange multiplier. The solution of equations $\left(\sum_{k=1}^{3N-6} y_k \exp(-\omega_k \lambda) \omega_k \right) = E_{if}$ yields the λ value. Lagrange's method for undetermined

multipliers gives the maximum of the product $\left[\prod_{k=1}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right) \right]$, which is the Franck-

Condon factor that fulfils the energy conservation condition $\left(\sum_{k=1}^{3N-6} n_k \omega_k - E_{if} \right) = 0$.

This approach also accounts for accepting modes with the $n_k > 1$, which became the crucially important accepting modes when the energy difference between the initial and final states (E_{if}) is large.

2.3. The anharmonic approximation

2.3.1. The X-H bonds anharmonicity

Previous studies showed that vibrational modes with large y_k values (>0.01) and energies larger than 1000 cm^{-1} provide large contributions to $\left[\prod_{k=1}^{3N-6} \left(\frac{e^{-y_k} y_k^{n_k}}{n_k!} \right) \right]$

[26, 27]. Vibrational X-H bond stretching modes with energies of about $2000\text{-}3000 \text{ cm}^{-1}$ have the largest contributions to b_j and t_j [26, 27]. In the harmonic approximation, the contributions to b_j from the X-H stretching modes are large when $n_j=1$, whereas it is negligible when $n_j>1$ due to the nature of the harmonic oscillator wave functions.

Anharmonic effects can be estimated by using the Morse oscillator, whose wave function is [38]

$$\psi_n(R) = N_n \exp(-z/2) z^{b_n/2} L_n^{b_n}(z) \quad (15),$$

where $z = 2\beta \exp(-\alpha[R - R_e])$, $b_n = 2\beta - 2n - 1$, $\beta = \frac{1}{\alpha} \sqrt{2mD}$. The D value is the dissociation energy, α is an anharmonicity constant, m is the reduced mass, R_e is

the equilibrium distance, $N_n = \left(\frac{\alpha b_n n!}{\Gamma(b_n + n + 1)} \right)^{1/2}$, $L_n^{b_n}(z)$ is the n :th Laguerre

polynomial, and $\Gamma(b_n + n + 1)$ is the gamma function. Parameters D and α can be obtained from the anharmonicity parameter χ and the energy ω as $D = \omega/4\chi$ and $\alpha = \sqrt{2\omega\chi}$. The dissociation energy of the X-H bonds is usually about ~ 4.5 eV and the typical vibrational energy (ω) of the X-H bonds is ~ 3300 cm^{-1} , yielding a χ value of 0.02 [28]. Almost the same χ value was recently used for estimating anharmonic contributions to the k_{IC} rate constant [25]. Using Eq. (15), one can derive an analytical expression for b_j [39]

$$b_j^2 = \frac{b_n b_0 \Gamma(2\beta - n)}{2\beta^2 \Gamma(2\beta)} D \quad (16).$$

The b_j value in Eq. (16) decreases slower with increasing n in comparison with the corresponding expression for b_j in the harmonic approximation in Eq. (10). We use Eq. (16) to estimate the anharmonic effects. The energy of the Morse oscillator is $E_j = \omega_j(n_j + 1/2) - \chi\omega_j(n_j + 1/2)^2$, which is used in Eq. (2) and Eq. (3). The t_j parameter can also be obtained by using the wave function of the Morse oscillator [40]:

$$t_j^2 = \frac{(B - n)N\Gamma(2B - n + 1)}{2n^2(2B - n)^2\Gamma(2B + 1)} \quad (17),$$

where $(B + 1/2)^2 = D$.

Using Eq. (16) and Eq. (17) yields significant contributions to b_j and t_j values even when $n_j > 1$. This gives the opportunity to calculate also P , P_j and $P_{jj'}$ for molecules with smaller energy gap than 25000 cm^{-1} , where anharmonic effects are less significant. The b_j and t_j parameters in the expressions for the IC rate constant have been calculated in the anharmonic approximation using Eq. (16) and Eq. (17) for only the strongly anharmonic X-H vibrational modes. P , P_j and $P_{jj'}$ were estimated using the fitting curves reported in Ref. [16]. $k_{IC}^{anh-fit}$ is then calculated using Eq. (4) and Eq. (5).

2.3.2. The anharmonicity of vibrational modes with $\omega > 1000$ cm^{-1} and associated bond stretching

The use of the Morse oscillator model is not very accurate for vibrational modes with energies in the range of $1000 \text{ cm}^{-1} < \omega < 3000 \text{ cm}^{-1}$. However, the Franck-Condon factors can still be estimated by considering vibrational modes associated with bond stretching. This approach has been used by Yeganeh and Ratner [41], since the Franck-Condon factors ($\langle 0|n \rangle$) can be calculated analytically in this case [41, 42]:

$$\langle 0|n \rangle = \zeta^{N/2} \left(\frac{2}{1+\zeta} \right)^{N-n} \frac{\Gamma(C-n)}{\Gamma(C-2n+1)} \sqrt{\frac{(C-2n)\Gamma(C-n+1)}{\Gamma(n+1)\Gamma(C)}} {}_2F_1(-n, C-n; C-2n+1, \frac{2}{1+\zeta}) \quad (18),$$

where ${}_2F_1(-n, N-n; N-2n+1, \frac{2}{1+\zeta})$ is hypergeometric function, $C = 2\sqrt{\frac{mD}{\alpha}} - 1$ and $\zeta = \exp(-\alpha[R_0^i - R_0^f])$, where $R_0^i - R_0^f$ is the difference in the equilibrium bond length of the initial and final states that can be obtained from the y value of each mode. Eq. (18) holds when $\alpha = \alpha^i = \alpha^f$ or when the shape of the potential energy surface is very similar for the initial and final electronic states.

The method of Lagrange multipliers was employed in calculations of k_{IC} using Eq. (16), Eq. (17) and Eq. (18) for b_j , t_j and the Franck-Condon factors, respectively. We also used a χ value of 0.02 as in Ref. [25]. We use the notation k_{IC}^{anh} for the IC rate constants that were obtained using this approach. All k_{IC} were calculated in the Herzberg-Teller approximation.

2.4. The non-adiabatic interaction induced mixture between S_1 and S_2 for naphthalene and anthracene

The mixture between S_1 and S_2 states induced by non-adiabatic interaction has recently been estimated for the tetraoxa[8]circulene and found to be very small [43], whereas the NACME is much larger for polyacenes [44]. Since the energy difference between S_1 and S_2 is small ($500\text{-}2500 \text{ cm}^{-1}$) [45], a high level of theory is required for estimating the NACME between these states, because the NACME can be of the same order as the energy gap. We used the BAGEL [46] software for

calculating $\langle \varphi_{S_2}(\vec{r}, \vec{s}, \vec{R}) \frac{\partial \varphi_{S_1}(\vec{r}, \vec{s}, \vec{R})}{\partial R_{vq}} \rangle_{|\vec{R}=\vec{R}_0}$. Finally $\langle \varphi(S_2) | \Lambda | \varphi(S_1) \rangle$ is estimated using $\langle \varphi_{S_2}(\vec{r}, \vec{s}, \vec{R}) \frac{\partial \varphi_{S_1}(\vec{r}, \vec{s}, \vec{R})}{\partial R_{vq}} \rangle_{|\vec{R}=\vec{R}_0}$ as well as Eq. (8) and Eq. (10) as in Ref. [43].

3. Calculation details

The molecular structure optimization, calculations of the second derivative of the potential energy surface (hessian) of the S_1 state, calculation of the first derivative of the potential energy surface (gradient) of the S_0 or S_2 states, calculations of the NACME between the S_1 and S_0 states, as well as calculations of spin-orbit coupling matrix elements (SOCME) between the S_1 state and an energetically lower triplet state were performed at the same level of theory as used in previous studies and described below [26, 27]. The molecular structures as well as the gradient and hessian calculations were performed for the lowest state at the density functional theory (DFT) and for the excited states - at the time dependent density functional theory (TDDFT) [47] level using the B3LYP [48] functional and the def2-TZVP [49] basis sets. The first-order NACMEs were calculated at the TDDFT level with the Turbomole code using perturbation theory [50, 51]. Spin-orbit coupling matrix elements $\langle S_1 | H_{SO} | T_i \rangle$ between the S_1 state and the i^{th} triplet states T_i being energetically below the S_1 state were calculated at the complete active space self-consistent field (CASSCF) level using Gamess-US [52, 53].

$\langle \frac{\varphi_i(\vec{r}, \vec{s}, \vec{R}) \partial^2 \varphi_f(\vec{r}, \vec{s}, \vec{R})}{\partial R_{vq} \partial R_{v'q'}} \rangle_{|\vec{R}=\vec{R}_0}$ and $(\frac{\partial(H_{SO}^{if})}{\partial R_{vq}})_{|\vec{R}=\vec{R}_0}$ were calculated numerically using a three-point finite-difference approximation with a step length of 0.05 Å along each Cartesian coordinate of the molecular structure.

Excitation energies calculated at the extended multi-configuration quasi-degenerate perturbation theory of second order (XMC-QDPT2) [54] level were used as zeroth-order values. The XMC-QDPT2 calculations were performed using the Firefly software [55]. The initial guess MOs were obtained at the Hartree–Fock level of theory for H₂TPP. The 5 highest occupied MOs and the 5 lowest

unoccupied MOs formed the active space in the CASSCF calculations, which were performed with state averaging over the four lowest electronic states. For the other molecules, we used the same active space as used in our previous works [26, 27].

In the calculation of $\langle \varphi(S_2) | \Lambda | \varphi(S_1) \rangle$, $\langle \varphi_{S_2}(\vec{r}, \vec{s}, \vec{R}) \frac{\partial \varphi_{S_1}(\vec{r}, \vec{s}, \vec{R})}{\partial R_{vq}} \rangle_{|\vec{R}=\vec{R}_0}$ was obtained at the XMC-CASPT2 level of theory using same active space and basis set as used in XMC-QPDT2 calculations on naphthalene and anthracene.

4. Results and discussions

4.1. Naphthalene and anthracene

Naphthalene fluoresces from the two lowest excited singlet states (S_1 and S_2) [35, 44, 45], which suggests that S_1 and S_2 are strongly coupled by the non-adiabatic interaction. The same might hold for anthracene. The calculated k_{IC} rate constants for naphthalene-h₈ and for deuterated naphthalene-d₈ are given in Table 1. The corresponding data for anthracene-h₁₀ and anthracene-d₁₀ are given in Table 2.

The rate constants have been calculated using the harmonic and anharmonic approximations. Table 1 shows that very small k_{IC} values are obtained when the harmonic approximation is used. The k_{IC}^{harm} rate constant for the $S_1 \rightarrow S_0$ transition of anthracene is two orders of magnitude smaller than k_{IC}^{anh} , whereas the rest of the k_{IC}^{harm} rate constants in Table 1 and 2 are several orders of magnitude smaller than the corresponding k_{IC}^{anh} rate constants.

The $k_{IC}^{anh-fit}$ and k_{IC}^{anh} rate constants for most transitions are of the same order of magnitude. The only exception is the rate constant for the $S_2 \rightarrow S_0$ transition of anthracene-d₁₀. The k_{IC} rate constant for the $S_2 \rightarrow S_0$ transition of naphthalene is significantly larger than for the $S_1 \rightarrow S_0$ transition, because the $S_1 \rightarrow S_0$ transition possesses some accepting modes with small y values. Naphthalene-d₈ has $k_{IC}^{anh-fit}$ and k_{IC}^{anh} rate constants for the $S_1 \rightarrow S_0$ transition that are two to three orders of magnitude smaller than for naphthalene-h₈. For the $S_2 \rightarrow S_0$ transition, the naphthalene-d₈ rate constants are one to two orders of magnitude smaller for than

for naphthalene-h₈. The significantly faster IC process of naphthalene-h₈ is due to the C-H accepting modes, whose vibrational energies of 3209 cm⁻¹ and 3228 cm⁻¹ are significantly larger than those for naphthalene-d₈.

Table 1. The calculated accepting modes (ω in cm⁻¹) and the IC rate constants (in s⁻¹) for the S₁(B_{3u})→S₀(A_g) and S₂(B_{2u})→S₀(A_g) transitions of naphthalene-h₈ and naphthalene-d₈. The irreducible representations of the electronic states are given in parenthesis. The Huang-Rhys factors (γ) and the irreducible representation (irrep) of the accepting modes are also given.

Transition	Accepting modes $\omega(y)$, irrep	$k_{IC}^{harm-fit}$	k_{IC}^{harm}	$k_{IC}^{anh-fit}$	k_{IC}^{anh}
naphthalene-h ₈					
S ₁ (B _{3u})→ S ₀ (A _g)	1417(0.18), A _g	4·10 ⁻⁸	6·10 ⁻¹⁴	1·10 ⁺¹	1·10 ⁺¹
	1478(0.10), B _{1g}				
	3209(5·10 ⁻⁴), B _{1g}				
	3228(9·10 ⁻⁴), A _g				
S ₂ (B _{2u})→ S ₀ (A _g)	1064(0.19), A _g	2·10 ⁻²	1·10 ⁻⁴	8·10 ⁺²	2·10 ⁺²
	1414(0.56), A _g				
	1624(0.44), B _{1g}				
naphthalene-d ₈					
S ₁ (B _{3u})→ S ₀ (A _g)	1410(0.31), A _g	8·10 ⁻⁹	3·10 ⁻¹⁶	8·10 ⁻²	1·10 ⁻²
	2367(2·10 ⁻⁴), B _{1g}				
	2379(5·10 ⁻⁴), A _g				
S ₂ (B _{2u})→ S ₀ (A _g)	1313(0.27)	1·10 ⁻²	3·10 ⁻⁵	2·10 ⁺¹	2·10 ⁺¹
	1396(0.36), A _g				
	1560(0.59), B _{1g}				

Table 2. The calculated accepting modes (ω in cm⁻¹) and the IC rate constants (in s⁻¹) for the S₁(B_{3u})→S₀(A_g) and S₂(B_{2u})→S₀(A_g) transitions of anthracene-h₁₀ and

anthracene-d₁₀. The irreducible representations of the electronic states are given in parenthesis. The Huang-Rhys factors (γ) and the irreducible representation (irrep) of the accepting modes are also given.

Transition	Accepting modes $\omega(\gamma)$, irrep	$k_{IC}^{harm-fit}$	k_{IC}^{harm}	$k_{IC}^{anh-fit}$	k_{IC}^{anh}
anthracene-h ₁₀					
$S_1(B_{2u}) \rightarrow S_0(A_g)$	1431(0.52), A _g				
	1543(0.17), B _{1g}	$2 \cdot 10^{+5}$	$1 \cdot 10^{+4}$	$6 \cdot 10^{+6}$	$4 \cdot 10^{+6}$
	1603(0.20), A _g				
$S_2(B_{3u}) \rightarrow S_0(A_g)$	1423(0.18), A _g				
	1521(0.10), A _g	$3 \cdot 10^{-1}$	$4 \cdot 10^{-7}$	$3 \cdot 10^{+5}$	$9 \cdot 10^{+4}$
	3207($7 \cdot 10^{-4}$), A _g				
anthracene-d ₁₀					
$S_1(B_{2u}) \rightarrow S_0(A_g)$	1427(0.38), A _g				
	1471(0.24), B _{1g}	$6 \cdot 10^{+1}$	$5 \cdot 10^{+3}$	$2 \cdot 10^{+5}$	$3 \cdot 10^{+5}$
	1575(0.31), A _g				
$S_2(B_{3u}) \rightarrow S_0(A_g)$	1384(0.03), A _g				
	1461(0.25), B _{1g}	$1 \cdot 10^{-1}$	$4 \cdot 10^{-9}$	$4 \cdot 10^{+2}$	$5 \cdot 10^{-1}$
	2375($2 \cdot 10^{-4}$), A _g				

The lowest excited state of anthracene belongs to the B_{2u} irreducible representation. Thus, the ¹B_{2u} and ¹B_{3u} states of anthracene appear in the opposite order as compared to naphthalene. The calculated excitation energies are compared to experimental data in Table 3. The calculations suggest that the T_1 and T_2 states of naphthalene and anthracene are energetically below the S_1 state.

The k_{IC} rate constant of anthracene is smaller for the $S_2 \rightarrow S_0$ transition than for the $S_1 \rightarrow S_0$ one regardless of the employed approximation. Deuteration decreases the k_{IC} values for the $S_2 \rightarrow S_0$ and the $S_1 \rightarrow S_0$ transitions of anthracene as well as of naphthalene. The isotope effect on the k_{IC} of the $S_1 \rightarrow S_0$ transition of anthracene-h₁₀ and anthracene-d₁₀ is the same order of magnitude. The calculations also show that

deuteration decreases the k_{IC} values, which is expected to lead to an increase in the quantum yield of fluorescence (ϕ_f), if the ISC rate constants (k_{ISC}) are the same for both isotopomers. (see Table 4). However, according to the experimental data, deuteration increases ϕ_f for naphthalene, but slightly decreases ϕ_f for anthracene [45, 56]. The calculated rate constants in Table 4 shows that k_{IC} of naphthalene is much smaller than $k_r(S_1 \rightarrow S_0)$ and $k_r(S_2 \rightarrow S_0)$ rates. Thus, the IC process has a very small effect on the quantum yield of naphthalene. The calculated ϕ_f yield for naphthalene of about 0.9 is also much larger than the experimental values of 0.24 and 0.42 for naphthalene-h₈ and naphthalene-d₈, respectively. The calculations provide too large quantum yields for naphthalene, and they also predict a too small isotope effect.

Table 3. Calculated excitation energies (E in cm⁻¹), oscillator strengths (f), matrix elements of perturbation operators (in cm⁻¹) for naphthalene-h₈, naphthalene-d₈, anthracene-h₁₀ and anthracene-d₁₀.

Property	Naphthalene	Anthracene
E(S ₁)	33500	23390
	32050 (exp) [45]	26610 (exp) [45]
E(S ₂)	36000	25890
	35000 (exp) [45]	27900 (exp) [35]
E(T ₁)	21534	12647
	21250 (exp) [45]	14900 (exp) [45]
E(T ₂)	32981	23128
E(T ₃)	37000	29040
$\langle \phi_{S_1} \hat{H}_{so} \phi_{T_1} \rangle$	2.47	2.00
$\langle \phi_{S_2} \hat{H}_{so} \phi_{T_2} \rangle$	0.29	0.001
$f(S_1 \rightarrow S_0)$	$1.6 \cdot 10^{-4}$	0.06
$f(S_2 \rightarrow S_0)$	0.06	$1.3 \cdot 10^{-4}$
	Naphthalene-h ₈	Anthracene-h ₁₀

$\langle \varphi(S_2) \Lambda \varphi(S_1) \rangle$	250	240
	Naphthalene-d ₈	Anthracene-d ₁₀
$\langle \varphi(S_2) \Lambda \varphi(S_1) \rangle$	50	240

Table 4. The calculated rate constants (in s⁻¹) and the quantum yield of fluorescence (φ_{fl}) for naphthalene-h₈, naphthalene-d₈, anthracene-h₁₀ and anthracene-d₁₀.

Parameter	Naphthalene-h ₈	Naphthalene-d ₈
$k_{IC}^{anh}(S_2 \rightarrow S_0)$	$2.0 \cdot 10^2$	$2.0 \cdot 10^1$
$k_{IC}^{anh}(S_1 \rightarrow S_0)$	$1.0 \cdot 10^1$	$1.0 \cdot 10^{-2}$
$k_{ISC}(S_1 \rightarrow T_1)$	$1.0 \cdot 10^4$	$1.0 \cdot 10^4$
$k_{ISC}(S_1 \rightarrow T_2)$	0	0
$k_{ISC}(S_2 \rightarrow T_2)$	$2.0 \cdot 10^6$	$2.0 \cdot 10^6$
$k_r(S_1 \rightarrow S_0)$	$1.2 \cdot 10^5$	$1.2 \cdot 10^5$
$k_r(S_2 \rightarrow S_0)$	$5.0 \cdot 10^7$	$5.0 \cdot 10^7$
φ_{fl}	>0.9	>0.92
$k_r^*(S_1 \rightarrow S_0)$	$7.0 \cdot 10^5$	$1.2 \cdot 10^5$
$k_{ISC}^*(S_1 \rightarrow T_2)$	$3.0 \cdot 10^6$	$5.0 \cdot 10^4$
φ_{fl}^*	0.19	0.67
φ_{fl} (exp) [45]	0.24	0.42
	Anthracene-h ₁₀	Anthracene-d ₁₀
$k_{IC}^{anh}(S_I \rightarrow S_0)$	$6 \cdot 10^6$	$3 \cdot 10^5$
$k_{ISC}(S_I \rightarrow T_1)$	$4 \cdot 10^3$	$4 \cdot 10^3$
$k_{ISC}(S_I \rightarrow T_2)$	0	0
$k_{ISC}(S_2 \rightarrow T_2)$	2.0	2.0
$k_r(S_I \rightarrow S_0)$	$2.0 \cdot 10^7$	$2.0 \cdot 10^7$
$k_r(S_2 \rightarrow S_0)$	$1.0 \cdot 10^5$	$1.0 \cdot 10^5$
$k_r^*(S_1 \rightarrow S_0)$	$2.0 \cdot 10^7$	$2.0 \cdot 10^7$

$k_{ISC}^*(S_1 \rightarrow T_2)$	1	1
φ_{fl}	0.76	0.98
φ_{fl}^*	0.18	0.33?
φ_{fl} (exp) [45]	0.67	0.10

It has been suggested that there is a non-adiabatic coupling between the S_1 and S_2 states for naphthalene [35, 44, 57], which significantly increases the ISC rate constant from the lowest singlet state to the second triplet state $k_{ISC}^*(S_1 \rightarrow T_2)$. Here the asterisk (*) denotes that S_1 is a mixture of the S_1 and S_2 states due to non-adiabatic coupling ($\varphi^*(S_1) = \varphi(S_1) + c_{12}\varphi(S_2)$). The c_{12} coefficient can be estimated using perturbation theory:

$$c_{12} = \frac{\langle \varphi(S_2) | \Lambda | \varphi(S_1) \rangle}{E(S_2) - E(S_1)} \quad (19)$$

The calculated $\langle \varphi(S_2) | \Lambda | \varphi(S_1) \rangle$ values are 250 cm^{-1} and 50 cm^{-1} yielding c_{12} coefficients of 0.1 and 0.02 for naphthalene- h_8 and naphthalene- d_8 , respectively. Computational levels with the high accuracy show that these values are typical for NACME between S_1 and S_2 states, when the non-adiabatic coupling is significant [58, 59, 60].

When the c_{12} mixing coefficient is considered, the rate constant for the radiative transition from the mixed S_1 state $k_r^*(S_1 \rightarrow S_0)$ of naphthalene- h_8 is $7.0 \cdot 10^5 \text{ s}^{-1}$ and $3.0 \cdot 10^5 \text{ s}^{-1}$ for naphthalene- d_8 . The ISC rate constant from the mixed S_1 state $k_{ISC}^*(S_1 \rightarrow T_2)$ is $3.0 \cdot 10^6 \text{ s}^{-1}$ for naphthalene- h_8 and $5.0 \cdot 10^4 \text{ s}^{-1}$ for naphthalene- d_8 . The $k_{ISC}(S_1 \rightarrow T_2)$ vanishes without non-adiabatic mixing of S_1 and S_2 . For the mixed S_1 and S_2 state, we obtain quantum yields of fluorescence (φ_{fl}^*) of 0.19 and 0.67 for naphthalene- h_8 and naphthalene- d_8 , which agree rather well with the experimental values of 0.24 and 0.42 [45]. The calculations show the importance of considering non-adiabatic coupling between the S_1 and S_2 states when estimating the fluorescence quantum yield of naphthalene.

For anthracene-h₁₀, our calculations without considering the non-adiabatic interaction yields $\phi_{fl}=0.87$, which agrees reasonably with the experimental value of 0.67 [45]. Thus, the IC process is the main non-radiative channel of the excited state, whereas the ISC process is much slower. The calculated $\langle \phi(S_2) | \Lambda | \phi(S_1) \rangle$ value of 240 cm⁻¹ for anthracene-h₁₀ and anthracene-d₁₀ yielded $c_{12} = 0.1$ for both isotopomers. Since $\langle \phi_{S_2} | \hat{H}_{so} | \phi_{T_2} \rangle$ is small, the non-adiabatic mixing does not significantly affect k_{ISC} . The rate constant of the radiative transition k_r and the IC rate constant k_{IC} are also unaffected by the mixing, because $k_r(S_1 \rightarrow S_0) \gg k_r(S_2 \rightarrow S_0)$ and $k_{IC}(S_1 \rightarrow S_0) \gg k_{IC}(S_2 \rightarrow S_0)$. The present calculations are not able to reproduce the experimentally observed anomalous deuteration effect of anthracene. The small energy difference between the S₁ and T₂ states may lead to a significant non-adiabatic coupling between them, whose strength may differ for the isotopomers. However, we are not aware of any software that could be employed to estimate this coupling.

Since the present algorithm gives the opportunity to accurately calculate k_{IC} for molecules with $E_{if} > 25000$ cm⁻¹, we have also considered benzene as a test case. For benzene, we obtained $k_{IC}^{anh-fit}$ of $1.2 \cdot 10^{-1}$ s⁻¹ and k_{IC}^{anh} of $3.2 \cdot 10^{-2}$ s⁻¹ for the S₁→S₀ transition with an energy difference of 43500 cm⁻¹ between the initial and final state. The accepting modes have vibrational energies of 3239 cm⁻¹ and 1034 cm⁻¹. The obtained results for benzene are in a good agreement with previously calculated values using a semi-empirical approach and with experimental data [35, 61].

4.2 H₂P and H₂TPP

Free-base tetraphenylporphyrin (H₂TPP) and free-base porphyrin (H₂P) are interesting molecules for studies of photophysical properties, because deuteration of the two inner protons have significant effects on the photophysical properties of H₂TPP and almost no effect on the photophysical properties of H₂P [45]. We have previously calculated rate constants for H₂P and H₂TPP using the different models

and levels of theory [20, 26, 27], whereas we compute here contributions to their rate constants and to the quantum yield of fluorescence from the anharmonicity and deuteration perspectives. The obtained results are collected in Tables 5 and 6. Some vibronic and spin-vibronic parameters are in good agreement with previous results [62, 63].

The harmonic and anharmonic approximations yield IC rate constants $k_{IC}^{harm-fit}$, $k_{IC}^{anh-fit}$ and k_{IC}^{anh} that are of about same magnitude, whereas k_{IC}^{harm} is much smaller. Anharmonicity is, in principle, not considered in the calculation of k_{IC}^{harm} and $k_{IC}^{harm-fit}$. However, in the calculation of $k_{IC}^{harm-fit}$ the fitting curves with average y values for the accepting modes consider to some extent the anharmonic effects, which are important for H₂P due to the presence of a strongly anharmonic accepting mode with an energy of 3627 cm⁻¹. Deuteration does not influence the $k_{IC}^{anh-fit}$ and k_{IC}^{anh} values even though the frequency of the accepting mode decreases. This is because the accepting mode of D₂P (with an energy of 1364 cm⁻¹) is upon deuteration excited with high quantum numbers, which compensates for the large energy shift of the second accepting mode from 3627 cm⁻¹ to 2660 cm⁻¹ for D₂P. The obtained results agree well with experimental data [45] and explain why the quantum yield of fluorescence (φ_{fl}) is the same for H₂P and D₂P. The IC process is the main deactivation channel of the S₁ state and the IC rate constant (k_{IC}) is not affected by the deuteration.

The main deactivation channel of the S₁ state of H₂TPP is internal conversion. H₂TPP and D₂TPP have different accepting modes, whereas they are the same for H₂P and D₂P. The vibrational mode corresponding to the accepting N-H stretch at 3630 cm⁻¹ in H₂TPP is not an accepting mode of D₂TPP, which has instead several modes with lower frequencies that contributes to the calculated FC factor leading to a smaller k_{IC} and φ_{fl} than for H₂TPP.

Table 5. The calculated accepting modes (ω in cm⁻¹) and the IC rate constants (in s⁻¹) for the S₁ → S₀ transition for the H₂P, H₂TPP, D₂P and D₂TPP. The Huang-Rhys

(HR) factors (y) and the irreducible representation (irrep) of the accepting modes are also given.

Molecule	Accepting modes ω , HR (y), irrep	$k_{IC}^{harm-fit}$	k_{IC}^{harm}	$k_{IC}^{anh-fit}$	k_{IC}^{anh}
H ₂ P	1364(0.04), B _{1g} 3627(1.6·10 ⁻⁴), A _g	8.0·10 ⁷	1.0·10 ¹	4.0·10 ⁸	8.0·10 ⁷
D ₂ P	1364(0.04), B _{1g} 2660(0.17), A _g	2.0·10 ⁶	0.5·10 ¹	4.0·10 ⁸	8.0·10 ⁷
H ₂ TPP	1558(0.02), A ₁ 3630(3.3·10 ⁻⁴), A ₁	4.0·10 ⁸	2.0·10 ¹	1.0·10 ⁹	9.0·10 ⁸
D ₂ TPP	1258(0.03), A ₁ 1285(0.03), A ₁ 1386(0.02), A ₁ 1558(0.02), A ₁	8.0·10 ⁷	2.0·10 ⁻¹	9.0·10 ⁷	2.0·10 ⁷

Table 6. Calculated excitation energies (E in cm⁻¹), spin-orbit coupling matrix elements (in cm⁻¹), rate constants (in s⁻¹) and fluorescence quantum yield (φ_f) for H₂P, H₂TPP, D₂P and D₂TPP.

	H ₂ P	D ₂ P	H ₂ TPP	D ₂ TPP
E(S ₁)	17000 16210 (exp) [45]	17000	16500 15340 (exp) [45]	16500
E(T ₁)	13000 12580 (exp) [45]	13000	11500 11640 (exp) [45]	11500
E(T ₂)	14517	14517	14517	14517
$\langle \varphi_{S_1} \hat{H}_{so} \varphi_{T_1} \rangle$	1.6	1.6	1.3	1.3
$\langle \varphi_{S_1} \hat{H}_{so} \varphi_{T_2} \rangle$	0.0	0.0	0.0	0.0

$k_{ISC}(S_1 \rightarrow T_1)$	$7.0 \cdot 10^6$	$7.0 \cdot 10^6$	$4.0 \cdot 10^6$	$4.0 \cdot 10^6$
$k_{ISC}(S_1 \rightarrow T_2)$	0.0	0.0	0.0	0.0
$k_r(S_1 \rightarrow S_0)$	$5.0 \cdot 10^6$		$2.0 \cdot 10^7$	
$k_{IC}^{anh}(S_1 \rightarrow S_0)$	$8.0 \cdot 10^7$	$8.0 \cdot 10^7$	$9.0 \cdot 10^8$	$9.0 \cdot 10^7$
φ_{fl}	0.08	0.08	0.02	0.18
φ_{fl} (exp) [45]	0.05	0.05	0.09	0.12

4.3. Tetraoxa[8]circulene and pyrromethene

To check the accuracy of our algorithm, we have calculated k_{IC} rate constants for tetraoxa[8]circulene (4B) and pyrromethene (PM567) and compared them to previously calculated IC rate constants that were obtained without considering anharmonic effects.

The obtained rate constants for 4B and PM567 are summarized in Table 7. For 4B, the anharmonic effects are small. The k_{IC}^{harm} rate constant is a factor of 2-10 times smaller than k_{IC}^{anh} and $k_{IC}^{anh-fit}$, whereas $k_{IC}^{harm-fit}$ that considers some anharmonic effects is in closer agreement with the k_{IC}^{anh} and $k_{IC}^{anh-fit}$ rate constants. $k_{IC}^{anh-fit}$ is a factor of 4 larger than k_{IC}^{anh} . Thus, the harmonic and anharmonic approximations leads to similar rate constants, because the accepting modes for 4B do not involve any X-H stretches.

One of the accepting modes of PM567 is the C-H stretch at 3062 cm^{-1} . The k_{IC} rate constant increases slightly when we consider anharmonic effects. However, the estimated the φ_{fl} value of 0.76 is high, since the radiative transition with k_r rate constant of $4 \cdot 10^{+7} \text{ s}^{-1}$ is the main deactivation channel of the S_1 state.

Table 7. The calculated accepting modes (ω in cm^{-1}) and the IC rate constants (in s^{-1}) for the $S_1 \rightarrow S_0$ transition of 4B and PM567. The Huang-Rhys (HR) factors (y) and the irreducible representation (irrep) of the accepting modes are also given.

Compound	Accepting modes ω , HR (y), irrep	$k_{IC}^{harm-fit}$	k_{IC}^{harm}	$k_{IC}^{anh-fit}$	k_{IC}^{anh}
4B	1276 (0.20), A_{1g}				
	1451(0.16), B_{1g}	$7.0 \cdot 10^6$	$4.0 \cdot 10^6$	$4.0 \cdot 10^7$	$1.0 \cdot 10^7$
	1702(0.78), A_{1g}				
PM567	1255(0.06), A_1	$1.0 \cdot 10^6$	$3.0 \cdot 10^4$	$9.0 \cdot 10^6$	$7.0 \cdot 10^6$
	3062($1.1 \cdot 10^{-3}$), A_1				

5. Summary and discussion

Computational methods for calculating rate constants of non-radiative transitions in the (Morse) anharmonic approximation have been developed and applied to naphthalene, anthracene, free-base porphyrin, free-base tetraphenylporphyrin, and their deuterated isotopomers, as well as to pyrometene and tetraoxa[8]circulene. The following conclusions can be drawn from the present calculations.

1. Anharmonic effects are important when calculating k_{IC} for transitions between electronic states that are energetically separated by more than 20000-25000 cm^{-1} . Rate constants $k_{IC}^{anh-fit}$ and k_{IC}^{anh} obtained using anharmonic models are quite accurate.

2. Anharmonic effects are also important when the energy difference between the initial and final states is smaller than 20000-25000 cm^{-1} , when the molecule contains an accepting X-H stretching modes with a vibrational energy larger than 2000 cm^{-1} . This is because the X-H vibrations can be accurately described only when anharmonic effects are considered. In these cases, the

anharmonic contributions to k_{IC} can be estimated already using the $k_{IC}^{harm-fit}$ model described in Ref. [26].

3. Calculations of k_{IC}^{harm} yielded accurate values for k_{IC} , when $E_{if} < 20000$ - 25000 cm^{-1} and there is at least one accepting mode with a sufficiently large Huang-Rhys factor ($y > 0.1$).

4. In the IC process of the studied molecules, the electronic excitation energy is converted into vibrational energy by exciting at least one of the X-H modes (b_j) and vibrational modes with large y values. For larger energy differences between the initial and final states, the X-H stretches are the main accepting vibrational modes, providing the main contribution to the b_j and P values.

Calculations of photophysical properties are still challenging. The accuracy of the electronic excitation energies obtained using modern state-of-the-art quantum chemistry methods is about 0.1 eV. Accurate calculations of the IC rate constants (k_{IC}) for molecules with small energy differences (E_{if}) between the initial and final state ($10000\text{ cm}^{-1} < E_{if} < 20000\text{ cm}^{-1}$) are difficult, because k_{IC} depends strongly on E_{if} . Explicit calculations of k_{IC} require studies of complicated physical phenomena such as the Herzberg-Teller effect [26], anharmonic effects, which are studied here, and the Duschinsky rotation [64], which can also significantly affect the rate constants. Hybrid methods involving semi-empirical or even empirical approaches in the computational scheme can be necessary and also useful. Recently, Humeniuk *et al.* formulated some rules of thumb for non-radiative transition rates [25]. They found for example that the Duschinsky rotation can strongly increase the k_{IC} value when the energy gap is large, whereas we here show that it is also very important to consider anharmonic effects in the calculation of k_{IC} . Duschinsky rotation is not accounted for in this work, which is the biggest shortcoming of our algorithm. Although recent studies showed that Duschinsky rotation can be important in calculations of k_{IC} [22-24, 65-68], comparisons of calculated and experimental values for the rate constants and quantum yields suggest that the Duschinsky contribution is relatively small for the rigid molecules

considered in this work. We plan though to implement Duschinsky rotation into our algorithm.

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