Research paper

Excitonic coupling effect on the nonradiative decay rate in molecular aggregates: Formalism and application

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ABSTRACT

We present here an analytical thermal vibration correlation function formalism to calculate the nonradiative decay rate constant (k_{nr}) considering excitonic coupling effect (ECE) for molecular aggregates based on split-operator approximation. Combining with first-principles calculations, we found that k_{nr} is enhanced by ECE for both H- and J-aggregates. In addition, ECE is found to be minor for the AIEgens (aggregation-induced emission luminogens).

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1. Introduction

Solid-phase photophysical processes determine the optical properties of organic luminescent materials, such as organic nanoparticles [1], thin films [2] and crystals [3]. The photophysical properties of organic molecular aggregates can be different from in solution phase due to a number of intermolecular interactions, such as excitonic coupling and electrostatic interaction, as well as charge transfer. [4] The excitonic coupling effect (ECE) on optical spectra has been widely investigated in organic molecular aggregates [5–13]. It has been long established that H-aggregate exhibits blue-shifted absorption and diminishingly weak (red-shifted) emission intensity, while J-aggregate presents red-shifted absorption and enhanced emission. [13,14] Nevertheless, our understanding of ECE on the nonradiative decay is extremely limited. Early, Freed claimed that the nonradiative transitions between the symmetric and antisymmetric Frenkel-exciton states are strictly forbidden by analyzing the nonadiabatic coupling through the zeroth-order representation [15]. Scharf and Dinur found that the nonradiative decay rate decreases drastically with aggregate size in the strong coupling limit for constant energy gap [16].

Huang and Rhys first proposed the quantitative non-radiative transition rate theory in F-centers by considering the strength of the coupling between the electron and the lattice [17]. Then, Lin [18], Jortner and Englman [19,20] extended the theory into the treatment of an isolated polyatomic molecule. In their treatments, the linear displaced oscillator model and the promoting-mode approximation were usually adopted. In recent years, in the context of understanding the aggregation-induced emission phenomena, we developed an analytical nonradiative transition rate theory with Dushinsky rotation effect [21,22] going beyond the promoting-mode approximation by using the thermal vibration correlation function (TVCF) approach [23]. TVCF is an analytical time-integrated rate formalism that can be efficiently solved by fast-Fourier transformation technique. All the vibrational modes and vibronic coupling at the molecular level can be taken into accounts. In this work, we further extended such analytical rate theory to tackle molecular aggregates by considering excitonic coupling effect within the Frenkel exciton model. By dividing the Hamiltonian into intra- and inter-molecular parts, we treat the latter by employing split-operator approximation. Then, it is convenient to construct TVCF and derive an analytical formula to calculate the nonradiative decay rate constant of an aggregate.

We then applied this formalism coupled with the hybrid quantum mechanics and molecular mechanics (QM/MM) calculations to explore the ECE on the nonradiative decay rate constants for a conjugated planar 2,3-dicyanopyrazino phenanthrene (DCPP) [24,25] as well as for four typical AIEgens (aggregation-induced emission luminogens), 2,3-dicyano-5,6-diphenylpyrazine (DCDPP) [26], 1,2-diphenyl-3,4-bis(diphenylmethylene)-1-cyclobutene (CB) [27,28], 1,1,2,3,4,5-hexaphenylsilole (HPS) [29,30], 1,1,3,4-tetraphenyl-2,5-bis(9,9-dimethylfluoren-2-yl)silole (BFTPS) [31,32], see Fig. 1.

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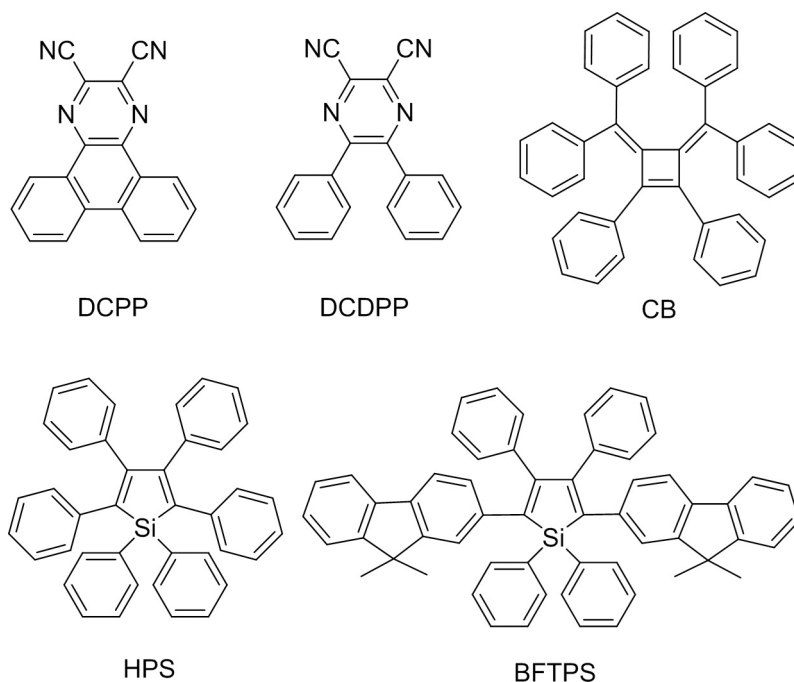   [1] These authors contributed equally.

Fig. 1. Molecular structures of the studied molecules.

These can provide a deeper understanding of the effect of intermolecular excited-state interaction on the luminescent property in organic molecular aggregates.

2. Formalism

In this section, we are going to derive an analytical nonradiative decay rate formalism for molecular aggregates in the weak coupling limit. Based on Fermi's Golden Rule (FGR), the nonradiative decay rate constant can be expressed as [21]

$$k_{nr} = \int_{-\infty}^{\infty} dt e^{i\Delta E t} \rho(t) \tag{1}$$

$$\rho(t) = \frac{1}{Z_e} \text{Tr}\left[e^{\frac{i\widehat{H}_0 t}{\hbar}} \widehat{H}' e^{\frac{-i\widehat{H}_0 t}{\hbar}} \widehat{H}' e^{-\beta \widehat{H}_e} \right] \tag{2}$$

where $\rho(t)$ is the TVCF of internal conversion. $\widehat{H}_0$ is the zeroth-order Hamiltonian. $\widehat{H}_e$ is the Hamiltonian of the initial state, which is the first excited state in the internal conversion process from S_1 to S_0. $\widehat{H}'$ is the Born-Oppenheimer (non-adiabatic) coupling arising from the nuclear kinetic term. ΔE is the energy difference between the initial and final states. Z_e is the partition function of the initial state. $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant and T the temperature.

Firstly, we take a dimer system to build the basis function, which reads

$$|\psi_1\rangle = |g(1)\rangle \otimes |g(2)\rangle, \quad |\psi_2\rangle = |e(1)\rangle \otimes |g(2)\rangle, \quad |\psi_3\rangle = |g(1)\rangle \otimes |e(2)\rangle, \tag{3}$$

where (1) and (2) are the first and second molecule of the dimer, respectively. Under Condon approximation, these can be recast as

$$|\psi_1\rangle = |g\rangle |Q_1 \otimes Q_2\rangle, \quad |\psi_2\rangle = |e_1\rangle |Q_1' \otimes Q_2\rangle, \quad |\psi_3\rangle = |e_2\rangle |Q_1 \otimes Q_2'\rangle, \tag{4}$$

where

$$|g\rangle = |\phi_{1g}\rangle \otimes |\phi_{2g}\rangle, \quad |e_1\rangle = |\phi_{1e}\rangle \otimes |\phi_{2g}\rangle, \quad |e_2\rangle = |\phi_{1g}\rangle \otimes |\phi_{2e}\rangle, \tag{5}$$

Q (Q') is the harmonic vibrational complete set at the ground (excited) state ϕ_{1g} (ϕ_{1e}) and ϕ_{2g} (ϕ_{2e}) are the electronic wave functions of molecule **1** and **2** at the ground (excited) state, respectively. Thus, the zeroth-order Hamiltonian for the dimer system can be expanded in the electronic wave function basis as

$$\widehat{H}_0 = \begin{bmatrix} \widehat{H}_{1g} + \widehat{H}_{2g} & 0 & 0 \\ 0 & \widehat{H}_{1e} + \widehat{H}_{2g} & J \\ 0 & J & \widehat{H}_{1g} + \widehat{H}_{2e} \end{bmatrix}, \tag{6}$$

and

$$\widehat{H}' = \sum_k \sum_n^2 [\langle e_n | \widehat{T}_{nk} | g \rangle + \langle e_n | \widehat{P}_{nk} | g \rangle \widehat{P}_{nk}](|e_n\rangle\langle g| + |g\rangle\langle e_n|). \tag{7}$$

Here, $\widehat{H}_{ng}$ ($\widehat{H}_{ne}$) is the harmonic Hamiltonian of the nth monomer at the ground (excited) state; J is the excitonic coupling; $\widehat{T}_{nk} = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial^2 q_{nk}}$ and $\widehat{P}_{nk} = -i\hbar \frac{\partial}{\partial q_{nk}}$ where q_{nk} is the normal coordinate of the kth normal mode for the nth monomer. The first term in Eq. (7) is much smaller than the second term in most cases and is often neglected [18]. Thus, Eq. (7) can be rewritten as

$$\widehat{H}' = \sum_k R_{1k}\widehat{P}_{1k}(|e_1\rangle\langle g| + |g\rangle\langle e_1|) + R_{2k}\widehat{P}_{2k}(|e_2\rangle\langle g| + |g\rangle\langle e_2|), \tag{8}$$

in which

$$R_{nk} \equiv \langle \phi_{ng} | \widehat{P}_{nk} | \phi_{ne} \rangle \tag{9}$$

is the intramolecular nonadiabatic coupling matrix elements (NACMEs). Inserting Eq. (6) into Eq. (2), the TVCF becomes