Consequences of coherence effects in nonradiative decay

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The manifestation of coherence effects in quantum yield measurements probing nonradiative decay is considered within the framework of effective Liouvillian dynamics. Special attention is given to the theoretical treatment of the quantum yield problem for the Freed-Jortner mesoscopic model for nonradiative decay. Exploiting the mathematical apparatus of dual Lanczos transformation theory, we obtain infinite-order analytic expressions for the fluorescence quantum yield and nonradiative decay rate of the initially prepared state and the quantum yields of hot fluorescence and hot phosphorescence.

I. INTRODUCTION

Treatments of nonradiative decay[1] based on the Markovian approximation to the relevant Hamiltonian subdynamics of a global effective Hamiltonian model with radiative damping[1,2] yield results that would lead one to believe that nonradiative transitions may serve as a mechanism for the storage of energy for an infinite period of time in isolated molecules that are optically excited and remain bounded. Given that molecules are always coupled to the free-radiation field, which plays the role of a dissipative sink, it seems that such energy storage is a physical impossibility. This suggests that there is something fundamentally wrong with the aforementioned Markovian approximation in some theories of nonradiative decay.[1] The purpose of this paper is to give a preliminary report of some infinite order analytic results based on effective Liouvillian dynamics that indicate that this is indeed the case due to the neglect of coherence effects. By coherence effects, we mean processes involving the transformation of phase coherences associated with the initially prepared state into other coherences and excitations in the system and their back reaction.

II. EFFECTIVE LIOUVILLIAN TREATMENT OF FREED-JORTNER MESOSCOPIC MODEL

In order to demonstrate the importance of coherence effects in nonradiative decay, let us consider the Freed-Jortner mesoscopic model,[1] which has played a central role as a prototype model in discussions of such decay. A schematic representation of this model is given in Fig. 1. $|\phi_s\rangle$ denotes some initially prepared state that carries oscillator strength to the ground state $|\phi_0\rangle$. The state $|\phi_s\rangle$ is coupled via the intramolecular interaction $\hat{U}$ to some densely packed but discrete states $\{|\phi_l\rangle\}$. All of the states are assumed to be radiatively damped. In the ab-

sence of the interaction $\hat{U}$ each of the states exhibit simple exponential radiative decay.

By definition, the quantum yield Φ^R for the radiation originating from the initially prepared state is given by

$$\Phi^R = \int_0^\infty dt\,[\Gamma^R(s,s)/\hbar]\rho(s,s;t)\ , \qquad (2.1)$$

where $\Gamma^R(s,s)/\hbar$ is the radiative decay rate of the state $|\phi_s\rangle$ and $\rho(s,s;t)$ is the probability for finding the system in this state at time t. It is convenient to write Φ^R as

$$\Phi^R = [\Gamma^R(s,s)/\hbar]\lim_{z\to 0+}\int_0^\infty dt\,\exp(-zt)\rho(s,s;t)\ , \qquad (2.2)$$

where the integral represents the Laplace transform of $\rho(s,s;t)$.

Adopting the effective Liouvillian dynamical model corresponding to the mesoscopic model depicted in Fig. 1, it is a straightforward exercise in projection operator algebra[3a,3b,4] to show that the temporal evolution of $\rho(s,s;t)$ may be described in terms of the non-Markovian equation of motion
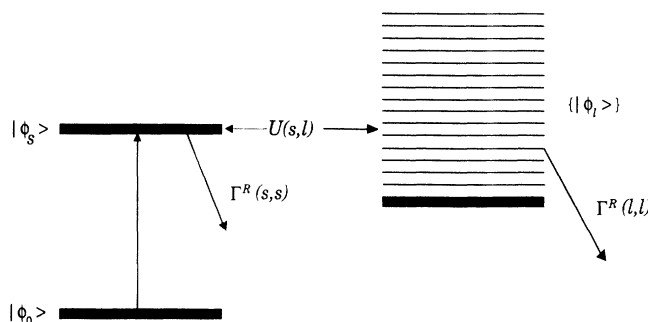

FIG. 1. Schematic representation of the Freed-Jortner mesoscopic model for nonradiative decay.

$$\frac{\partial}{\partial t}\rho(s,s;t) = -[\Gamma^R(s,s)/\hbar]\rho(s,s;t)$$
$$- \int_0^t dt' K(s,s;s,s;t-t')\rho(s,s;t') , \qquad (2.3)$$

where

$$K(s,s;s,s;t-t')$$
$$= -(N_{ss}^\dagger|\hat{L}_{PQ}\exp[-\hat{L}_{QQ}(t-t')]\hat{L}_{QP}|N_{ss}) .$$
$$(2.4)$$

In the above, $\hat{L}_{PQ}=\hat{P}\hat{L}\hat{Q}$, $\hat{L}_{QP}=\hat{Q}\hat{L}\hat{P}$, and $\hat{L}_{QQ}=\hat{Q}\hat{L}\hat{Q}$, where $\hat{L}$ is the transition operator embodying the details of the mesoscopic model.

The Hermitian projection operator

$$\hat{P} = |N_{ss})(N_{ss}^\dagger| \qquad (2.5)$$

projects onto that part P of the global dynamical vector space embedded with information about the population of the state $|\phi_s\rangle$. The Hermitian projection operator

$$\hat{Q} = \sum_l [\,|N_{sl})(N_{sl}^\dagger| + |N_{ls})(N_{ls}^\dagger|\,] + \sum_{l,l'} |N_{ll'})(N_{ll'}^\dagger| \qquad (2.6)$$

projects onto that part Q of the global dynamical vector space embedded with information about the phase coherence between the state $|\phi_s\rangle$ and the manifold $\{|\phi_l\rangle\}$, the phase coherence within the manifold $\{|\phi_l\rangle\}$, and the population of the $\{|\phi_l\rangle\}$ manifold. $\hat{P}$ and $\hat{Q}$ satisfy the usual relations $\hat{P}+\hat{Q}=\hat{I}$, $\hat{P}^2=\hat{P}$, $\hat{Q}^2=\hat{Q}$, and $\hat{P}\hat{Q}=\hat{Q}\hat{P}=\hat{0}$, where $\hat{0}$ is the null operator and $\hat{I}$ is the identity operator for the global dynamical vector space.

The dynamical vectors $\{|N_{jk})\}$ appearing in Eqs. (2.4)–(2.6) correspond to the operators $\{\hat{N}_{jk}=|\phi_j\rangle\langle\phi_k|\}$, where $\{|\phi_j\rangle\}$ are the basis vectors in the Freed-Jortner mesoscopic model. The left dynamical vector $(N_{jk}^\dagger|$ and the right dynamical vector $|N_{jk})$ are connected by the relation $(N_{jk}^\dagger|=|N_{jk})^\dagger$.

Making use of Eqs. (2.2) and (2.3), we find that the quantum yield Φ^R for the radiation originating from the initially prepared state is given by

$$\Phi^R = K_R/(K_R+K_{NR}) , \qquad (2.7)$$

where $K_R = [\Gamma^R(s,s)/\hbar]$ is the radiative decay rate and

$$K_{NR} = \lim_{z\to 0+} \mathcal{H}(s,s;s,s;z) \qquad (2.8)$$

is the nonradiative decay rate, with

$$\mathcal{H}(s,s;s,s;z) = -(N_{ss}^\dagger|\hat{L}_{PQ}(z\hat{Q}+\hat{L}_{QQ})^{-1}\hat{L}_{QP}|N_{ss}) \qquad (2.9)$$

denoting the Laplace transform of the memory kernel $K(s,s;s,s;t)$.

As far as quantum yield measurements are concerned, Eq. (2.8) is an exact expression for the nonradiative decay rate K_{NR} independent of whether or not the initially prepared state $|\phi_s\rangle$ exhibits exponential decay. Of course, the nonradiative decay rate given by Eq. (2.8) must be equal to the nonradiative decay rate deduced from time-resolved photon counting measurements when exponential decay is obtained.

In order to obtain insight into the various contributions to the nonradiative decay rate K_{NR} and to construct an infinite order expression for this rate, we find it convenient to partition the projection operator $\hat{Q}$ [see Eq. (2.6)] as follows:

$$\hat{Q} = \hat{Q}_1 + \hat{Q}_2 , \qquad (2.10)$$

where

$$\hat{Q}_1 = \sum_l \hat{Q}_1^{(l)} \qquad (2.11)$$

and

$$\hat{Q}_2 = \sum_{l,l'} \hat{Q}_2^{(ll')} , \qquad (2.12)$$

with

$$\hat{Q}_1^{(l)} = |N_{sl})(N_{sl}^\dagger| + |N_{ls})(N_{ls}^\dagger| + |N_{ll})(N_{ll}^\dagger| \qquad (2.13)$$

and

$$\hat{Q}_2^{(ll')} = |N_{ll'})(N_{ll'}^\dagger| . \qquad (2.14)$$

The projection operator $\hat{Q}_1$ projects onto the subspace Q_1 bearing information about the phase coherence between the state $|\phi_s\rangle$ and the manifold $\{|\phi_l\rangle\}$ and the population of the manifold $\{|\phi_l\rangle\}$. [See Eqs. (2.11) and (2.13).] The projection operator $\hat{Q}_2$ projects onto the subspace Q_2 bearing information about the phase coherence within the manifold $\{|\phi_l\rangle\}$. [See Eqs. (2.12) and (2.14).]

A diagrammatic representation of the subspaces P, Q_1, and Q_2 and their coupling with each other is given in Fig. 2. Some of the terms giving rise to coherence effects in the diagram of Fig. 2 are enumerated and classified in Fig. 3. Note that we have classified these terms as describing first-order coherence effects, second-order coherence effects without interferences, and second-order coherence effects with interferences. The interferences correspond to processes in which the phase coherences between the state $|\phi_s\rangle$ and the individual states of the manifold $\{|\phi_l\rangle\}$ interfere due to the coupling of these coherences to a common coherence within the manifold $\{|\phi_l\rangle\}$.

Making use of the above-described partitioning, we write Eq. (2.9) as follows:

$$\mathcal{H}(s,s;s,s;z) = -(N_{ss}^\dagger|\hat{L}_{PQ_1}[z\hat{Q}_1+\hat{L}_{Q_1Q_1}^{EFF}(z)]^{-1}\hat{L}_{Q_1P}|N_{ss}) \qquad (2.15a)$$

$$= -\sum_{l,l'} (N_{ss}^\dagger|\hat{L}_{PQ_1^{(l)}}[z\hat{Q}_1+\hat{L}_{Q_1Q_1}^{EFF}(z)]^{-1}\hat{L}_{Q_1^{(l')}P}|N_{ss}) , \qquad (2.15b)$$

where

$$\hat{L}\,^{EFF}_{Q_1 Q_1}(z) = \hat{L}_{Q_1 Q_1} + \hat{L}_{Q_1 Q_2}(z\hat{Q}_2 + \hat{L}_{Q_2 Q_2})^{-1}\hat{L}_{Q_2 Q_1} \tag{2.16a}$$

$$= \sum_l \hat{L}_{Q_1^{(l)} Q_1^{(l)}} + \sum_{l,l'} \hat{L}_{Q_1^{(l)} Q_2}(z\hat{Q}_2 + \hat{L}_{Q_2 Q_2})^{-1}\hat{L}_{Q_2 Q_1^{(l')}} \tag{2.16b}$$

is the effective transition operator for the subspace Q_1 with the z dependence arising from the coupling of this subspace to the subspace Q_2. The interactions contributing to Eqs. (2.15a)–(2.16b) are described by the diagrams in Figs. 2 and 3.

Inspection of the terms describing coherence effects suggests that first-order coherence effects are more important than second-order coherence effects. Assuming this to be the case, we write [see Eqs. (2.15a)–(2.16b) and Figs. 2 and 3]

$$\mathcal{H}(s,s\,;s,s\,;z) = \sum_l \mathcal{H}^{(l)}(s,s\,;s,s\,;z)\;, \tag{2.17}$$

where

$$\mathcal{H}^{(l)}(s,s\,;s,s\,;z) = -(N_{ss}^\dagger|\hat{L}_{PQ_1^{(l)}}(z\hat{Q}\,_1^{(l)} + \hat{L}_{Q_1^{(l)} Q_1^{(l)}})^{-1}\hat{L}_{Q_1^{(l)} P}|N_{ss})\;. \tag{2.18}$$

Exploiting the mathematical apparatus of dual Lanczos transformation theory[3], one can readily show that $\mathcal{H}^{(l)}(s,s\,;s,s\,;z)$ may be written in the form of the rational function[3b,3c]

$$\mathcal{H}^{(l)}(s,s\,;s,s\,;z) = [2|U(s,l)|^2/\hbar]\{[\hbar z + d_+(s,l)]^2 - d_-(s,l)[\hbar z + d_+(s,l)]\}$$

$$\times \{[\hbar z + d_+(s,l)]^3 - d_-(s,l)[\hbar z + d_+(s,l)]^2 + \Delta(s,l)[\hbar z + d_+(s,l)] - d_-(s,l)\epsilon(s,l)^2\}^{-1}\;, \tag{2.19}$$

where $d_\pm(s,l) = (\frac{1}{2})[\Gamma^R(s,s) \pm \Gamma^R(l,l)]$, $\epsilon(s,l) = \xi_s - \xi_l$, and $\Delta(s,l) = 2|U(s,l)|^2 + \epsilon(s,l)^2$, with ξ_s and ξ_l denoting the energies of the states $|\phi_s\rangle$ and $|\phi_l\rangle$, respectively.

Taking the $z \to 0+$ limit of the spectral function $\mathcal{H}(s,s\,;s,s\,;z)$, we obtain the following infinite-order expression for the nonradiative decay rate:

$$K_{NR} = (2/\hbar)\sum_l |U(s,l)|^2 d_+(s,l)/\{\epsilon(s,l)^2 + d_+(s,l)^2 + 2|U(s,l)|^2 d_+(s,l)/[d_+(s,l) - d_-(s,l)]\}\;. \tag{2.20}$$

This result combined with Eq. (2.7) provides us with an infinite-order expression for the quantum yield Φ^R for the radiation originating from the initially prepared state.

FIG. 2. Diagrammatic representation of the subspaces P, Q_1, and Q_2 and their coupling with each other for the Freed-Jortner mesoscopic model. [See discussion of Eqs. (2.15a)–(2.16b).] The solid lines represent the interaction between superstates.

FIG. 3. Diagrammatic representation of some of the terms giving rise to coherence effects in the diagram of Fig. 2 and their classification. See caption of Fig. 2 for definition of symbols.

For $\epsilon(s,l)^2 + d_+(s,l)^2 \gg 2|U(s,l)|^2 d_+(s,l)/[d_+(s,l) - d_-(s,l)]$ for all l, Eq. (2.20) assumes the weak-coupling form[5]

$$K_{NR} = (2/\hbar) \sum_l |U(s,l)|^2 d_+(s,l)/[\epsilon(s,l)^2 + d_+(s,l)^2] \ .$$

(2.21)

The above result may be regarded as a variant of the result[1b]

$$K_{NR} = 2 \ \text{Re} \ \mathcal{H}_{\mathcal{H}}(s,s;\xi)$$

(2.22)

obtained when the Markovian approximation is imposed on the relevant Hamiltonian subdynamics of the global effective Hamiltonian model. In the above,

$$\mathcal{H}_{\mathcal{H}}(s,s;\xi) = (1/\hbar) \sum_l |U(s,l)|^2/[i(\xi + \xi_l) + (\tfrac{1}{2})\Gamma^R(l,l)] \ ,$$

(2.23)

where ξ is the energy parameter appearing in effective Hamiltonian theories.[1]

It should be clear that Eq. (2.20) is at a higher level of approximation than Eq. (2.22), which neglects coherence effects altogether. Equation (2.20) includes first-order coherence effects to infinite order in the interaction $\hat{U}$ between the state $|\phi_s\rangle$ and the manifold $\{|\phi_l\rangle\}$. Moreover, Eq. (2.20) is exact for a two-state system.

If we let the manifold $\{|\phi_l\rangle\}$ become completely dark, i.e., $\Gamma^R(l,l) = 0$ for all l, we find that the result given by Eq. (2.20) for K_{NR} vanishes. Then $\Phi^R = 1$. This result is consistent with our earlier assertion that nonradiative transitions cannot serve as a mechanism for the storage of energy for an infinite period of time in isolated molecules that are optically excited and remain bounded. Clearly, the result given by Eq. (2.22) is inconsistent with this and only requires $\hat{U}$ to be nonvanishing in order to obtain $\Phi^R < 1$. In sharp contrast, Eq. (2.20) requires the widths of the states in the manifold $\{|\phi_l\rangle\}$ to be nonvanishing in order to obtain $\Phi^R < 1$ (see Fig. 4). Of course,

these widths $\{\Gamma(l,l)\}$ may be due to the coupling of the $\{|\phi_l\rangle\}$ manifold to both radiative and nonradiative (dissociative, collisional, etc.) dissipative continua. [In general, $d_\pm(s,l) = \tfrac{1}{2}[\Gamma(s,s) \pm \Gamma(l,l)]$, where $\Gamma(s,s)$ and $\Gamma(l,l)$ are the total width of the states.]

It is easy to show that the quantum yield $\Phi^{R'}$ for the radiation originating from the manifold $\{|\phi_l\rangle\}$ is given by $\Phi^{R'} = K_{NR}/(K_R + K_{NR})$ when radiative decay is the only open dissipative channel for an isolated molecule that remains bounded. As one might expect, the quantum yields Φ^R and $\Phi^{R'}$ conform to the relation $\Phi^R + \Phi^{R'} = 1$. If the manifold $\{|\phi_l\rangle\}$ is comprised of singlet and triplet states, we can partition K_{NR} as $K_{NR} = K_{IC} + K_{ISC}$, where K_{IC} and K_{ISC} are the internal conversion and intersystem crossing rates, respectively. K_{IC} (K_{ISC}) may be obtained from Eq. (2.20) by simply restricting the sum over all l to run over all singlet (triplet) electronic-nuclear states. Then the quantum yield $\Phi^{R'}$ may be written $\Phi^{R'} = \Phi^{IC} + \Phi^{ISC}$, where $\Phi^{IC} = K_{IC}/(K_R + K_{IC} + K_{ISC})$ and $\Phi^{ISC} = K_{ISC}/(K_R + K_{IC} + K_{ISC})$, respectively, denote the quantum yields for hot fluorescence and hot phosphorescence.

Second-order coherence effects without interferences [see Figs. 2 and 3]. may be readily incorporated into Eq. (2.20) with the aid of dual Lanczos transformation theory.[3] The inclusion of these effects leads to an expression for the nonradiative decay rate K_{NR} that is identical in structure to Eq. (2.20) with $\epsilon(s,l)$ and $d_+(s,l)$ replaced by the renormalized forms

$$\tilde{\epsilon}(s,l) = \epsilon(s,l) + \Delta\epsilon(s,l)$$

(2.24)

and

$$\tilde{d}_\pm(s,l) = d_\pm(s,l) + \Delta d(s,l) \ ,$$

(2.25)

where

$$\Delta\epsilon(s,l) = - \sum_{l' (\neq l)} |U(s,l')|^2 \epsilon(l',l)/[\epsilon(l',l)^2 + d_+(l',l)^2]$$
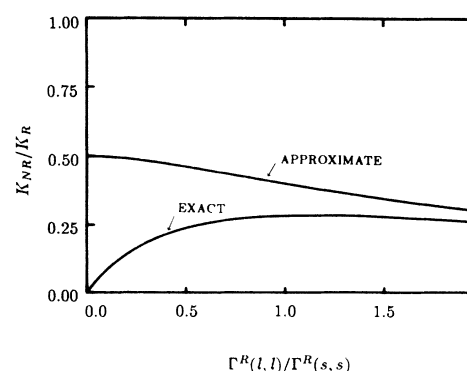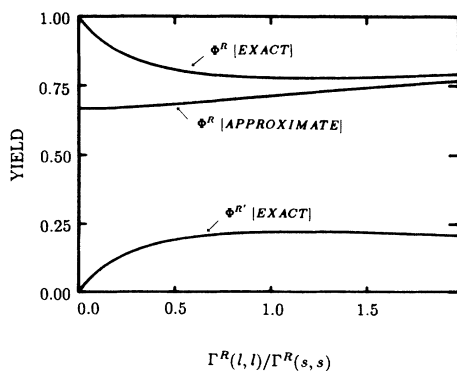
(2.26)

and

FIG. 4. Comparison of exact and approximate weak-coupling results for the radiative quantum yield Φ^R and nonradiative decay rate K_{NR} of the initially prepared state $|\phi_s\rangle$ of a two-state system for which $[\epsilon(s,l)^2/|U(s,l)|^2] = 1.0$ and $[\Gamma^R(s,s)^2/|U(s,l)|^2] = 4.0$. The radiative quantum yield $\Phi^{R'}$ for for the state $|\phi_l\rangle$ is also displayed.

$$\Delta d(s,l)= \sum_{l'\,(\neq l)} |U(s,l')|^2 d_+(l',l)/[\epsilon(l',l)^2+d_+(l',l)^2] \,,$$

$$(2.27)$$

with $d_\pm(l',l)=\frac{1}{2}[\Gamma(l',l')\pm\Gamma(l,l)]$ and $\epsilon(l',l)=\xi_{l'}-\xi_l$.

Apart from introducing energy shifts $\{\Delta\epsilon(s,l)\}$ and additional broadening $\{\Delta d(s,l)\}$, the basic structure of Eq. (2.20) is preserved when $\epsilon(s,l)$ and $d_\pm(s,l)$ are replaced by the renormalized forms $\tilde{\epsilon}(s,l)$ and $\tilde{d}_\pm(s,l)$. The physics discussed earlier is essentially the same provided the

system remains bounded in the $\{|\phi_l\rangle\}$ manifold. If some of these states become unbounded in the infinite volume limit, as in the case of dissociation, the physics dramatically changes. The contribution $2|U(s,l_u)|^2\tilde{d}_+(s,l_u)/[\tilde{d}_+(s,l_u)-\tilde{d}_-(s,l_u)]$ made by the unbounded state $|\phi_{l_u}\rangle$ to the properly renormalized form Eq. (2.20) vanishes in the infinite volume limit. Then the contribution K_u made by the unbounded states to the nonradiative decay rate K_{NR} assumes the form

$$K_u=(2/\hbar)\int d\xi_{l_u}\rho(\xi_{l_u})|U(s,l_u)|^2\tilde{d}_+(s,l_u)/[\tilde{\epsilon}(s,l_u)^2+\tilde{d}_+(s,l_u)^2] \,,\qquad(2.28)$$

where $\rho(\xi_{l_u})$ is the density of states for the unbounded part $\{|\phi_{l_u}\rangle\}$ of the $\{|\phi_l\rangle\}$ manifold. Clearly, K_u is nonzero even when the states $\{|\phi_{l_u}\rangle\}$ are radiatively dark and not coupled to any other continua, i.e., when $d_\pm(s,l_u)=(\frac{1}{2})\Gamma(s,s)$ or the bare widths $\{\Gamma(l_u,l_u)\}$ vanish. [Of course, the renormalized form $\tilde{d}_+(s,l_u)$ appears in Eq. (2.28).] Then the radiative quantum yield Φ^R for the initially prepared state is less than unity due to the fact that the states $\{|\phi_{l_u}\rangle\}$ assume the role of a truly dissipative continuum in the absence of additional damping.

Another attractive feature of our results is that they bridge the gap between the adiabatic and nonadiabatic regimes.[6] More specifically, we find that when the condition

$$2|U(s,l)|^2\tilde{d}_+(s,l)/[\tilde{d}_+(s,l)-\tilde{d}_-(s,l)]$$

$$\gg\tilde{\epsilon}(s,l)^2+\tilde{d}_+(s,l)^2$$

is satisfied for some state $|\phi_l\rangle$, the contribution made by that state to the properly renormalized form of Eq. (2.20) is given by $[\Gamma(l,l)/\hbar]$, i.e., the contribution made by the state $|\phi_l\rangle$ is given by the rate at which it decays via dissipative processes. Recent experiments[7] on photo-induced intramolecular electron transfer in polar solvents appear to be in agreement with this result.

III. CONCLUDING REMARKS

In this paper, we demonstrated the important role played by coherence effects in nonradiative decay by treating the quantum yield problem for the Freed-Jortner

mesoscopic model[1] within the framework of effective Liouvillian dynamics. It was shown that the treatment based on the Markovian approximation to the relevant Hamiltonian subdynamics is at best a weak-coupling approximation to the effective Liouvillian treatment due to the discarding of dynamical information about coherence effects. In fact, we found that the former approach is not equivalent to the effect Liouvillian treatment even for a two-state system. Our results suggest that, in general, treatments of photophysical phenomena based on the Markovian approximation to a Hamiltonian subdynamics must be viewed with some caution and that they may lead to results endowed with wrong physics.

Exploiting the mathematical apparatus of dual Lanczos transformation theory,[5] we obtained infinite-order analytic expressions for the radiative quantum yield and nonradiative decay rate for the initially prepared state in the Freed-Jortner mesoscopic model.[1] Also, we obtained infinite-order analytic expressions for the quantum yields of hot fluorescence and hot phosphorescence. Models involving a detailed description of intramolecular interactions and dissipative processes may be readily substituted into our results for computational studies. Another attractive feature of our results is that they bridge the gap between the adiabatic and nonadiabatic regimes[6] in a manner that is consistent with experiment.[7]

ACKNOWLEDGMENTS

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