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Spontaneous Emission and Nonadiabatic Electron Transfer Rates in Condensed Phases

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In this paper we explore the non-Condon effect of fluctuations of the tunneling matrix element caused by a condensed medium on the rates of nonadiabatic electron transfer (ET) and spontaneous emission from an excited electronic state. For a charge-transfer complex immersed in a polar polarizable liquid, the solvent effect renormalizes the ET matrix element due to (i) the instantaneous field of the solvent nuclear polarization and (ii) equilibrium solvation by the electronic solvent polarization. Fluctuations of the classical electric field of the solvent affect the form of the preexponential factor in the ET rate constant. In the new expression for the rate preexponent the vacuum ET matrix element is multiplied by the factor θ forming an effective ET matrix element in condensed phases. The parameter θ is controlled by the magnitude and orientation (relative to the differential solute dipole) of the diabatic transition dipole of the charge-transfer complex. The theory predicts a possibility of localization of the transferred electron when θ becomes equal to zero. The same treatment is applied to the rate of spontaneous radiative electronic transitions. We find that the product of the transition frequency and the adiabatic transition dipole is invariant in all solvents when (i) the diabatic transition dipole is collinear to the differential solute dipole moment and (ii) the spectral shift due to dispersion solvation is small. Under the same conditions, the adiabatic transition dipole in condensed phases and the effective ET matrix element are related by the Mulliken−Hush equation that becomes exact in our treatment.

1. Introduction

Electron transfer (ET) proceeds as quantum tunneling between two electronic states localized at the donor and acceptor sites. A condensed environment solvates the donor and acceptor resulting in two major effects: (i) the energy levels shift relative to each other and (ii) the tunneling probability is modified by the medium field resulting in the solvent dependence of the ET matrix element. The present paper is concerned with the latter focusing on the effect of electronic solvation and nuclear fluctuations on the ET matrix element and on the rates of radiationless and optical transitions. We provide a unified description of these two phenomena resulting in explicit relations between optical parameters and thermal activation properties.

The condition of tunneling in a quantum system is the equality of two eigenvalues of the system Hamiltonian. When a thermally fluctuating nuclear subsystem is involved, this requirement is usually formulated in terms of the Born−Oppenheimer (BO) decoupling ansatz leading to the condition of resonance between two electronic terms $E_i^{\mathrm{BO}}(\{Q_j\})$, $i = 1, 2$ at the same nuclear configuration $\{Q_j\}$: $E_1^{\mathrm{BO}}(\{Q_j\}) = E_2^{\mathrm{BO}}(\{Q_j\})$. Yet it does not provide the whole picture when the electronic subsystem of the solvent is included. The electric field of the transferred electron polarizes electronic shells of the solvent molecules creating electronic polarization in the solvent. The latter affects back the electron localized at the donor and acceptor sites shifting the corresponding electronic energies. Because of the self-consistent character of this solvation effect, the calculation of electronic energies becomes a nontrivial problem.[1−4] The problem simplifies when the bound solvent electrons are much faster than the transferred electron.[5] This implies that the frequency ω_s of the electronic excitations of the solvent is much higher than the frequency ω_0 associated with the vacuum adiabatic energy gap $\Delta J = \hbar\omega_0$ between the donor and acceptor electronic states. In this case, the transferred electron, like a small molecular polaron, is “dressed” by the equilibrium field of the solvent bound electrons that adiabatically follow the redistribution of the electronic density between the two states. In order to include equilibrium solvation by the solvent electrons the BO surfaces should be replaced by the (partial) *free* energies

$$\exp[-\beta E_i(\{Q_j\})] = \mathrm{Tr}_{\{\mathrm{el}\}}(\exp[-\beta H_i]) \tag{1}$$

obtained by averaging the system density matrix $\exp[-\beta H_i]$ over the solvent electronic degrees of freedom. In eq 1, $\mathrm{Tr}_{\{\mathrm{el}\}}$ is the trace over the electronic subsystem of the solvent, H_i is the diabatic Hamiltonian of the solute and the solvent, and $\beta = 1/(k_{\mathrm{B}}T)$.[6] Electronic transitions thus proceed between the diabatic states $E_i(\{Q_j\})$ as a result of nuclear fluctuations leading to the resonance condition $E_1(\{Q_j\}) = E_2(\{Q_j\})$.

This scheme is realized under the requirement of timescale separation

$$\omega_{\mathrm{n}} \ll \omega_0 \ll \omega_{\mathrm{s}} \tag{2}$$

where ω_{n} is the characteristic frequency of the nuclear modes. [For a continuum spectrum of nuclear modes, the upper cut-off frequency should be considered as ω_{n}]. For nonadiabatic ET, this picture naturally leads to the golden-rule expression for the rate constant.[7] Yet, before writing it down, we turn our attention to the physical concept of how the medium affects the electronic subsystem.

The solvation effect of the condensed medium on the ET system is commonly associated with the interaction of the solute charge distribution with the solvent field **E**. For a dipolar solute, the solute-solvent interaction term in the electronic Hamiltonian

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reads

$$-\hat{\mathbf{m}}_0\cdot\mathbf{E}$$

where $\hat{\mathbf{m}}_0$ is the solute electric dipole operator. [Note that $\hat{\mathbf{m}}_0$ need not be a point dipole.] The diagonal matrix elements of the electronic Hamiltonian yield the electronic energy levels. These energies are shifted from their vacuum values due to the diagonal solvation terms $-\mathbf{m}_{0i}\cdot\mathbf{E}$, where $\mathbf{m}_{0i}$ is the solute dipole moment representing the solute charge distribution in the ith state, $i=1, 2$. Fluctuations of the medium field eventually result in the resonance of the two localized states at which electronic transition may occur. Further, the off-diagonal matrix elements of the electronic Hamiltonian give us the ET matrix elements. The off-diagonal matrix element of the electronic Hamiltonian contains also the off-diagonal solvation term

$$-\mathbf{m}_0^{12}\cdot\mathbf{E}$$

where $\mathbf{m}_0^{12}$ is the transition dipole. As a result, the ET matrix element will depend on the fluctuating solvent field and, hence, will fluctuate itself. Of course, the off-diagonal matrix element $-\mathbf{m}_0^{12}\cdot\mathbf{E}$ is small compared to the diagonal one, $-\mathbf{m}_{0i}\cdot\mathbf{E}$. However, in the same way, the ET matrix element is small compared to the electronic energies for nonadiabatic transitions. One might expect that the relative effect of the off-diagonal solvation term on the ET matrix element is of the same order as the effect of the diagonal solvation term on the electronic energy levels. The goal of this paper is to quantify this effect. As we show below, a condensed medium really modifies substantially the preexponential factor of the nonradiative (ET) rate constant and the adiabatic transition dipole of the radiative transition. The two quantities turn out to be connected by an analog of the Mulliken−Hush relation that becomes exact when the solvent effect is correctly taken into account for both quantities.

The dependence of the ET matrix element on the nuclear subsystem in usually neglected in the Condon approximation fixing the ET matrix elements at a constant set of solvent nuclear coordinates. In this terminology, our desire here is to examine non-Condon effects due to fluctuations of the ET matrix element produced by the fluctuating classical electric field of the condensed medium. We do not consider here the coupling of the ET matrix element to quantum skeletal vibrations of the solute usually related to corrections to the Condon approximation.[8a,b] We will also assume the stationary limit in which the homogeneous broadening $\hbar\omega_n$ is much lower than the inhomogeneous broadening σ usually connected to the ET classical reorganization energy λ_{cl} by the relation: $\sigma^2 = 2\lambda_{cl}k_BT$. Therefore, the dynamical corrections to the Condon approximation[8c−e] are not considered here.

The preceding is intended to clarify the basic physics employed in the present paper. In fact, as we will see below, the effect of the condensed medium on the ET matrix element is more complex and is determined by two major factors: (i) instantaneous field of the solvent nuclear subsystem modifying the tunneling barrier[2,4b−d] and (ii) equilibrium solvation by the solvent electronic polarization reducing the tunneling probability by a Franck−Condon factor.[1a,2d,4f,9] Because of the first component, the ET matrix element $\tilde{V}_{12}(\{Q_j\})$ depends on the solvent nuclear configuration and the nonadiabatic rate constant reads

$$k_{ET}^{(i)} = (2\pi/\hbar)\langle|\tilde{V}_{12}(\{Q_j\})|^2\delta(\Delta E(\{Q_j\}))\rangle_i \qquad (3)$$

In eq 3,

$$\Delta E(\{Q_j\}) = E_2(\{Q_j\}) - E_1(\{Q_j\})$$

$$\langle...\rangle_i = Z_i^{-1}\int ...\exp[-\beta E_i(\{Q_j\})]\,d\Gamma$$

$$Z_i = \int \exp[-\beta E_i(\{Q_j\})]\,d\Gamma, \quad d\Gamma = dQ_1...dQ_N$$

and integration runs over the configurations of N solvent molecules. The superscript i in the rate constant $k_{ET}^{(i)}$ refers to the equilibrium distribution over which the averaging $\langle...\rangle_i$ is performed; $i=1$ for the forward ($1 \rightarrow 2$) reaction and $i = 2$ for backward ($2 \rightarrow 1$) ET. Equation 3 is of course a well-known one differing from the classical Levich theory[7] only through the dependence of the ET matrix element on the solvent configuration.

The rate constant given by eq 3 will form the basis for our development in section 2.2 below. The explicit dependence of $|\tilde{V}_{12}(\{Q_j\})|$ on the nuclear configuration will be given in section 2.1 in terms of a two-state solute model. Two-state models (or the equivalent description in terms of the spin−boson Hamiltonian) have been widely used in ET[1d,e,2d,3] and optical spectroscopy[10−14] applications. The two-state description is easily extended to an arbitrary number of solute electronic states[15] and, in fact, the nonadiabatic ET rate constant derived in section 2.2 is not restricted to two states. The time-separation requirement given by eq 2 usually forms the basis for constructing theories of nonadiabatic ET. Our development will be more general. The nonadiabatic rate constant is derived in section 2.2 for an arbitrary ratio of the solute and solvent characteristic frequencies ω_0 and ω_s, under the only requirement that they are quantum frequencies much higher than the classical frequency ω_n

$$\omega_n \ll \omega_0 \qquad \omega_n \ll \omega_s$$

We will show that the only consequence of removing the restriction $\omega_0 \ll \omega_s$ is the renormalization of the ET matrix element in the form of the Franck−Condon factor of shifted oscillators associated with the solvent electronic polarization.

The problem closely related to the solvent renormalization of the ET matrix element is the controversial question of the solvent dependence of the transition dipole of optical transitions. We address this point in section 2.3, where we derive expressions for transition dipoles and emission lifetimes. Finally, our results are summarized in section 3 where we show that a unified treatment of nonadiabatic ET reactions and optical transitions is possible in terms of an effective ET matrix element and the equilibrium adiabatic transition dipole.

2. Nonradiative and Radiative Rates

2.1. Two-Level Solute. Descriptions of intramolecular ET and optical transitions are essentially isomorphic.[16−18] We therefore use here a formulation applicable to both problems. The solute is considered to possess a dipole moment $\mathbf{m}_{01}$ in the initial state changing to $\mathbf{m}_{02}$ with electronic transition (the subscript "0" throughout below refers to the solute). The Hamiltonian of the two-state solute immersed in a polar polarizable liquid can be written as[18]

$$H_0 = \sum_{i=1}^{2}[I_i - \mathbf{m}_{0i}\cdot(\mathbb{E}_p + \mathbb{E}_e)]\,a_i^+ a_i + [V_{12} - \mathbf{m}_0^{12}\cdot(\mathbb{E}_p + \mathbb{E}_e)](a_1^+a_2 + a_2^+a_1) \qquad (4)$$

Here, a_i^+ and a_i are the creation and annihilation operators in the ith state with the diabatic vacuum energy I_i shifted by the interaction of the diabatic solute dipole $\mathbf{m}_{0i}$ with the instantaneous fields of the molecular fixed, $\mathbb{E}_p$, and induced, $\mathbb{E}_e$, charges. Similarly, the vacuum ET matrix element V_{12} is affected by the solvent field due to a nonzero diabatic transition dipole moment $\mathbf{m}_0^{12}$.

The transition moment $\mathbf{m}_0^{12}$ is the off-diagonal matrix element $\mathbf{m}_0^{12} = \langle\varphi_1|\hat{\mathbf{m}}_0|\varphi_2\rangle$ of the solute electric dipole moment operator $\hat{\mathbf{m}}_0$ taken in the vacuum diabatic basis $\{\varphi_1, \varphi_2\}$. In a broad sense, the orientation of $\mathbf{m}_0^{12}$ is not totally defined, since the transformation $\varphi_i \rightarrow -\varphi_i$, which does not affect observables, reverses the direction of the transition dipole $\mathbf{m}_0^{12} \rightarrow -\mathbf{m}_0^{12}$. However, the same transformation switches also the sign of V_{12}. The sign of the ET matrix element by itself does not have any physical meaning (although it does make sense to think of a sign switch with, for example, the nature of the donor−acceptor bridge[19a,b] or in a hopping sequence in a superexchange ET pathway[19c]). Nevertheless, the combination $V_{12} - \mathbf{m}_0^{12}\cdot(\mathbb{E}_p + \mathbb{E}_e)$ is meaningful, since both V_{12} and $\mathbf{m}_0^{12}$ change in the same way under the sign switch $\varphi_i \rightarrow -\varphi_i$. In fact, as we will see below, the observable quantities such as the ET rate constant and the transition moment depend on the ratio of the projection of $\mathbf{m}_0^{12}$ on the differential solute dipole and V_{12}. This ratio is invariant under the switch $\varphi_i \rightarrow -\varphi_i$ and hence the quantities based on it are physically meaningful.

The *diabatic* transition dipole $\mathbf{m}_0^{12}$ should not be confused with the *adiabatic* transition dipole $\mathbf{M}_0^{12}$ that is usually considered in optical spectroscopy of charge transfer complexes.[10,14] In the two-state model, the transition moment $\mathbf{M}_0^{12}$ is the off-diagonal matrix element of the electric dipole operator taken on adiabatic wave functions diagonalizing the vacuum solute Hamiltonian $H_0(\mathbb{E}_p = 0, \mathbb{E}_e = 0)$ (see the appendix)

$$\mathbf{M}_0^{12} = \mathbf{m}_0^{12}\frac{\Delta I}{\Delta J} - \Delta\mathbf{m}_0\frac{V_{12}}{\Delta J} \tag{5}$$

Here, $\Delta\mathbf{m}_0 = \mathbf{m}_{02} - \mathbf{m}_{01}$ is the differential solute dipole and ΔJ is the adiabatic vacuum energy gap

$$\Delta J = J_2 - J_1, \quad J_i = \frac{1}{2}[I_1 + I_2 \mp \sqrt{(I_1 - I_2)^2 + 4|V_{12}|^2}] \tag{6}$$

with "−" and "+" referring to $i = 1$ and $i = 2$, respectively.[20] A linear transformation of the diabatic basis can be used to diagonalize the diabatic dipole moment matrix leading to $m_0^{12} = 0$.[21] Such a transformation complicates the two-state Hamiltonian 4 and we will not pursue this approach here (see section 3.1 below).

Now we need to specify the solvent Hamiltonian H_s. Following Gehlen et al.,[3] we give it in the form of two harmonic collective modes, $\mathbb{E}_p$ and $\mathbb{E}_e$,

$$H_s = \frac{1}{4\mu_p}\mathbb{E}_p^2 + \frac{1}{4\mu_e}[\mathbb{E}_e^2 + \omega_s^{-2}\,\mathbb{E}_e^2] = U[\mathbb{E}_p, \mathbb{E}_e] + \frac{1}{4\mu_e\omega_s^2}\ddot{\mathbb{E}}_e^2 \tag{7}$$

Since the field $\mathbb{E}_p$ is a slow nuclear mode (according to the left inequality in eq 2), we excluded a corresponding kinetic energy term from eq 7 (BO decoupling). The kinetic energy is however retained for the fast quantum mode $\mathbb{E}_e$.[22]

The response functions μ_e and μ_p in eq 7 have been chosen so that the equilibrium chemical potentials of solvation of the dipole m_{0i} by electronic and nuclear subsystems are $\mu_e m_{0i}^2$ and $\mu_p m_{0i}^2$, respectively. In the continuum solvent description the response functions for spherical solutes are given in terms of the Onsager reaction field as

$$\mu_e = \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1}\frac{1}{R_0^3} \tag{8}$$

and

$$\mu_p = \left[\frac{\epsilon_s - 1}{2\epsilon_s + 1} - \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1}\right]\frac{1}{R_0^3} \tag{9}$$

where R_0 is the cavity radius and ϵ_∞ and ϵ_s are, respectively, the high-frequency and static dielectric constants of the solvent.

The potential energy term in eq 7 can be obtained from a more general molecular-based Hamiltonian of the solvent bath H_B by projecting out the two collective modes $\mathbb{E}_p$ and $\mathbb{E}_e$

$$\exp(-\beta U\,[\mathbb{E}_p, \mathbb{E}_e]) = \int \delta[\mathbb{E}_p(\{Q_j\}) - \mathbb{E}_p] \times \delta\,[\mathbb{E}_e(\{Q_j\}) - \mathbb{E}_e]\exp[-\beta H_B]\prod_{j=1}^{N} \mathrm{d}\dot{Q}_j\,\mathrm{d}Q_j \tag{10}$$

The cumulant expansion in eq 10 truncated after the second cumulant[23] will result in the Hamiltonian 7. The details of the molecular model and approximations used in averaging affect only the definitions of the response functions μ_p and μ_e. Once these are specified, a molecular description will be equivalent to that of eq 7.[24]

The whole system Hamiltonian $H = H_0 + H_s$ as given by eqs 4 and 7 is equivalent to that of a molecular polaron, i.e., an electron in either of two states coupled to an optical medium phonon.[1a,b] The free energy of the molecular polaron can be found under very general assumptions according to the following procedure.[1a,b] First a canonical transformation $\exp[iL]H\exp[-iL]$ usual for polaron and exciton problems[25] is applied to the system Hamiltonian H. The transformation with $L \propto (a_1^+a_1 - a_2^+a^2)\,\mathbb{P}_e$ ($\mathbb{P}_e = \dot{\mathbb{E}}_e/2\mu_e\omega_s^2$ is the momentum conjugate to $\mathbb{E}_e$) removes the solute−solvent interaction term in the Hamiltonian H and changes the basis of the solvent from that of a harmonic oscillator to a coherent state of a displaced oscillator. Then the infinite order perturbation expansion over the hopping Hamiltonian is used.[1a] This expansion can be summed under the assumption of the quantum character of the solvent electronic excitations $\beta\hbar\omega_s \gg 1$. The instantaneous *free* energy E^e of the two-state system equilibrated to the quantum field $\mathbb{E}_e$ and depending on the nuclear configuration $\{Q_j\}$ becomes[1a]

$$E^e = (E_1 + E_2)/2 - \beta^{-1}\ln[2\cosh(\beta\Delta\tilde{E}/2)] \tag{11}$$

where

$$\Delta\tilde{E} = \sqrt{\Delta E^2 + 4|\tilde{V}_{12}|^2} \tag{12}$$

In eqs 11 and 12, the energy gap $\Delta E = E_2 - E_1$ is between the two diabatic energies E_i (eq 1) defined in our model (eqs 4 and 7), by the relation

$$E_i = I_i - \mathbf{m}_{0i}\cdot\mathbb{E}_p + E_i^{np} \tag{13}$$

E_i^{np} specifies the nonpolar potential arising as a result of averaging over the electronic solvent polarization. It includes the dispersion solute−solvent potential E_i^{disp} and the induction free energy $F_i^{\mathrm{e}} = \mu_{\mathrm{e}} m_{0i}^2$ of the interaction of the solvent-induced dipoles with the solute permanent dipole

$$E_i^{\mathrm{np}} = E_i^{\mathrm{disp}} + F_i^{\mathrm{e}} \tag{14}$$

When the timescale separation 2 is used in calculating the dispersion term, we get $E^{\mathrm{disp}} = -\mu_{\mathrm{e}}|m_0^{12}|^2$.[18,26] This expression is of the zeroth order in the ratio $\omega_0/\omega_{\mathrm{s}}$, $\omega_0 = \Delta J/\hbar$ neglecting the retardation effects of solvation by the bound solvent electrons.[4b] In this limit, E^{disp} is independent of the solute state and $\Delta E^{\mathrm{disp}} = E_2^{\mathrm{disp}} - E_1^{\mathrm{disp}}$ is equal to zero. A more accurate result can be obtained by implementing the Drude oscillator model for the solute induced dipole[18] or in the framework of the quantum perturbation theory.[27] Both approaches lead to the London form of the dispersion potential depending on the solute state even for a two-state solute. We discuss this in greater detail elsewhere[18] and now just label the dispersion potential with the subscript *i* indicating the dependence on the solute state.

The renormalized ET matrix element $\tilde{V}_{12}$ in eq 12 includes two physically different components. First, it is affected by the instantaneous field of the permanent solvent dipoles and equilibrium solvation by the induced dipoles[18]

$$V_{12}^{\mathrm{eff}} = V_{12} - \mathbf{m}_0^{12}\cdot\mathbb{E}_{\mathrm{p}} - 2\mu_{\mathrm{e}}(\mathbf{m}_0^{12}\cdot\bar{\mathbf{m}}_0) \tag{15}$$

where $\bar{\mathbf{m}}_0 = (\mathbf{m}_{01} + \mathbf{m}_{02})/2$. Second, ET results in a displacement of quantum oscillators representing molecular polarizability. The ET matrix element acquires hence a Franck−Condon factor of the displaced oscillators[1,2d,4f,9,28]

$$\tilde{V}_{12} = V_{12}^{\mathrm{eff}} \exp\left[-\frac{1}{2}S_{\mathrm{e}}\right], \quad S_{\mathrm{e}} = \frac{\mu_{\mathrm{e}}\Delta m_0^2}{\hbar\omega_{\mathrm{s}}} \tag{16}$$

An expression analogous to eqs 15 and 16 has been obtained by Kim and Hynes[2d] in terms of the diagonal and off-diagonal matrix elements of the solute electric field interacting with continuum solvent polarization.

The ET matrix element given by eqs 15 and 16 should be substituted into eqs 11 and 12 to give the instantaneous free energy E^{e} for an arbitrary ratio $\omega_0/\omega_{\mathrm{s}}$ not restricted to the time-separation condition 2. The exponential factor S_{e} renormalizing V_{12}^{eff} to $\tilde{V}_{12}$ disappears in the limit $\omega_{\mathrm{s}} \to \infty$ implying that the only difference between the effect of an arbitrary quantum field $\mathbb{E}_{\mathrm{e}}$ and a field much faster than the solute electron (in terms of eq 2) is the appearance of the renormalization factor $\exp[-{}^1/_2 S_{\mathrm{e}}]$ in the ET matrix element. This result, obtained first for molecular polarons,[1a] has been recently rederived by Song and Stuchebrukhov in application to ET.[28] In their treatment, the renormalization of the hopping matrix element is caused by a continuum spectrum of solvent modes with frequencies higher than a quantum cut-off frequency ω_{q}

$$S'_{\mathrm{e}} = 2\int_{\omega_{\mathrm{q}}}^{\infty} \frac{J(\omega)}{\omega^2}\frac{\mathrm{d}\omega}{\pi}$$

where $J(\omega)$ is the spectral density of harmonic oscillators modeling the thermal bath. The cut-off frequency ω_{q} has been attributed in ref 28b to the effective frequency of quantum skeletal vibrations of the solute instead of the electronic excitation frequency ω_{s} in the present formulation. As a result, S'_{e} becomes higher than S_{e} further lowering the effective ET matrix element ("induced nonadiabaticity"[28b]). There is actually no contradiction between the two descriptions. In the golden-rule expression for the rate constant the transformation from S_{e} to S'_{e} is achieved by including the Franck−Condon factor of skeletal solute vibrations resulting in an additional contribution to the exponential renormalization in $\tilde{V}_{12}$.

The transition from the ω_{s} cut-off frequency in our present treatment to ω_{q} in ref 28 is a special case of the general rescaling procedure adiabatically eliminating oscillators with high frequencies by renormalizing the hopping matrix element.[29] The process may be continued to a finite renormalized hopping matrix element with $\omega_{\mathrm{q}} \to 0$. For subohmic, $J(\omega) \propto \omega^s$ ($s < 1$), and, under additional conditions, ohmic, $J(\omega) \propto \omega$, forms of the spectral density the rescaling results in the phenomenon of localization when $\tilde{V} \to 0$ with lowering temperature.[29] In the derivation presented in the next section we demonstrate a possibility of localization at high temperatures when V_{12}^{eff} passes through zero due to the solvation terms in eq 15.

The analysis performed above is easily generalized to a solute with more than two electronic levels $i = 1, ..., n$.[18] Equation 13 remains intact in this case and the effective matrix element between the states *i* and *j* becomes[15,18]

$$V_{ij}^{\mathrm{eff}} = V_{ij} - \mathbf{m}_0^{ij}\cdot\mathbb{E}_{\mathrm{p}} - 2\mu_{\mathrm{e}}(\mathbf{m}_0^{ij}\cdot\bar{\mathbf{m}}_0)$$

Therefore, the rate constant of nonadiabatic ET between the states $i = 1$ and $j = 2$ derived in the next section is not limited to a two-state solute and is equally suited to solutes with an arbitrary number of electronic states.

2.2. ET Rate Constant. Now we calculate the nonadiabatic rate constant from the golden-rule expression 3 and eqs 13−16. The averaging of the δ-function in eq 3 is performed by using the common representation

$$\langle|\tilde{V}_{12}|^2\delta(\Delta E)\rangle_i = \int_{-\infty}^{\infty}(\mathrm{d}\xi/2\pi)\langle|\tilde{V}_{12}|^2 \exp[i\xi\Delta E]\rangle_i \tag{17}$$

Above we have projected out two solvent fields $\mathbb{E}_{\mathrm{p}}$ and $\mathbb{E}_{\mathrm{e}}$ from the whole manifold of the system degrees of freedom and then integrated over $\mathbb{E}_{\mathrm{e}}$ to get the diabatic free energies and the renormalized ET matrix element. The averaging in eq 17 thus reduces to that over the inertial[30] field $\mathbb{E}_{\mathrm{p}}$

$$\langle f[\mathbb{E}_{\mathrm{p}}]\rangle_i = (\beta/4\pi\mu_{\mathrm{p}})^{1/2}[-\beta\mu_{\mathrm{p}}m_{0i}^2]\int f[\mathbb{E}_{\mathrm{p}}] \exp\left[-(\beta\mathbb{E}_{\mathrm{p}}^2/4\mu_{\mathrm{p}}) + \beta\mathbf{m}_{0i}\cdot\mathbb{E}_{\mathrm{p}}\right] \mathrm{d}\mathbb{E}_{\mathrm{p}} \tag{18}$$

If we omit the solvent dependence of $\tilde{V}_{12}$ and put $\tilde{V}_{12} = V_{12}$, eqs 3, 17, and 18 give the well-known[7] expression for the nonadiabatic ET rate

$$k_{\mathrm{NA}}^{(i)} = A_{\mathrm{NA}}\mathrm{FC}(\Delta F_i), \quad \mathrm{FC}(\Delta F_i) = \exp\left[-\beta\frac{\Delta F_i^2}{4\lambda_{\mathrm{p}}}\right] \tag{19}$$

Here, $\lambda_{\mathrm{p}} = \mu_{\mathrm{p}}\Delta m_0^2$ is the reorganization energy of the inertial solvent polarization,

$$A_{\mathrm{NA}} = \frac{|V_{12}|^2}{\hbar}\left(\frac{\pi\beta}{\lambda_{\mathrm{p}}}\right)^{1/2} \tag{20}$$

$$\Delta F_i = \Delta I + \Delta E^{\mathrm{np}} - 2\mu_{\mathrm{p}}(\Delta\mathbf{m}_0\cdot\mathbf{m}_{0i})$$

and $\Delta E^{\mathrm{np}} = E_2^{\mathrm{np}} - E_1^{\mathrm{np}}$ is according to eq 14.

The energies ΔF_i have a simple connection to optical spectroscopy defining the wavenumbers $\bar{\nu}_i$ of absorption ($i = 1$) and fluorescence ($i = 2$) transitions shifted from the vacuum gap $hc\bar{\nu}_0 = \Delta I$ by differential dispersion solvation[31] $hc\Delta\bar{\nu}^{\mathrm{disp}} = \Delta E^{\mathrm{disp}}$ and the effect of induced and permanent dipoles

$$hc\Delta\bar{\nu}_i^{\mathrm{p}} = -2\mu_{\mathrm{p}}(\Delta\mathbf{m}_0\cdot\mathbf{m}_{0i}) \mp \Delta F^{\mathrm{e}}$$

where "$-$" and "$+$" refer to $i = 1$ and $i = 2$, respectively. The total transition energy is thus

$$\Delta F_i = hc\bar{\nu}_i = hc[\bar{\nu}_0 + \Delta\bar{\nu}^{\mathrm{disp}} + \Delta\bar{\nu}_i^{\mathrm{p}}]$$

The Franck−Condon factor FC(ΔF_i) in eq 19 is easily generalized to include quantum skeletal vibrations of the solute.[32]

When the ET matrix element 16 is used in eqs 3, 17, and 18, we get a Gaussian integral over the inertial field $\mathbb{E}_{\mathrm{p}}$. The integration is straightforward resulting in the nonadiabatic rate constant given by eq 19 where the preexponential factor A_{NA} should now be replaced by the relation

$$A_i = \frac{\exp[-S_{\mathrm{e}}]}{\hbar}\left(\frac{\pi\beta}{\lambda_{\mathrm{p}}}\right)^{1/2} [|V_{12}\theta_i|^2 + 2\beta^{-1}\mu_{\mathrm{p}}|(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}})|^2] \qquad (21)$$

The parameter θ_i in eq 21 determines the deviation of the effective ET matrix element in condensed phases from the vacuum value V_{12}. For general orientations of the ground and excited state solute dipoles, it is given by the expression

$$\theta_i = 1 - \frac{(\mathbf{m}_0^{12}\cdot\hat{\mathbf{z}})}{\Delta m_0 V_{12}}(\Delta I + \Delta E^{\mathrm{disp}}) - \frac{\Delta E_{x,i}}{V_{12}} \qquad (22)$$

with

$$\Delta E_{x,i} = (\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}})(\mu_{\mathrm{e}}[\hat{\mathbf{x}}\cdot(\mathbf{m}_{01} + \mathbf{m}_{02})] + 2\mu_{\mathrm{p}}(\mathbf{m}_{0i}\cdot\hat{\mathbf{x}}))$$

Equation 22 simplifies for collinear $\boldsymbol{m}_{0i}$ to[33]

$$\theta = 1 - \frac{(\mathbf{m}_0^{12}\cdot\hat{\mathbf{z}})}{\Delta m_0 \mathrm{V}_{12}}(\Delta I + \Delta E^{\mathrm{disp}}) \qquad (23)$$

In eqs 21−23, $\hat{\mathbf{z}} = \Delta\mathbf{m}_0/\Delta m_0$ and $\hat{\mathbf{x}}$ is a unit vector perpendicular to $\hat{\mathbf{z}}$ in the plane formed by $\Delta\boldsymbol{m}_0$ and $\mathbf{m}_0^{12}$.

Equation 21 shows that two factors cause electronic transitions when $\Delta\boldsymbol{m}_0$ and $\mathbf{m}_0^{12}$ are not collinear: (i) tunneling coupling with the strength $|V_{12}\theta_i|$ between the diabatic states (the first summand in the brackets in eq 21) and (ii) thermal fluctuations ($\propto k_{\mathrm{B}}T$) of the solvent polarization in the direction perpendicular to the z-axis of redistribution the electronic density (the second summand in the brackets in eq 21). The solvent effect on the preexponential factor is controlled by two parameters: S_{e} and $\mathbf{m}_0^{12}$. S_{e} is small for the usual ET conditions and may be omitted in most cases. $\mathbf{m}_0^{12}$ is a vector and both the angle between $\Delta\mathbf{m}_0$ and $\mathbf{m}_0^{12}$ and the magnitude m_0^{12} determine the extent of deviation of the rate constant preexponential factor from the prediction of eq 20: we recover eq 20 for $\mathbf{m}_0^{12} = 0$.

If $\mathbf{m}_0^{12}$ is directed along the z-axis, we have $(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) = 0$ and eq 23 suggests an interesting phenomenon of self-localization of the transferred electron when $\theta = 0$. The condition for this to occur is

$$m_0^{12}(\Delta I + \Delta E^{\mathrm{disp}}) = \Delta m_0 V_{12} \qquad (24)$$

Equation 24 can be rewritten in the two-state model using the vacuum adiabatic transition dipole 5 yielding (ΔE^{disp} is usually negative[23b])

$$M_0^{12}\Delta I = -m_0^{12}\Delta E^{\mathrm{disp}}$$

In the case when the dispersion shift is negligeable (recall that $\Delta E^{\mathrm{disp}} = 0$ for a two-state solute with $\omega_0 \ll \omega_{\mathrm{s}}$), the above condition transforms to $M_0^{12} = 0$ implying that self-localization occurs when the vacuum adiabatic transition dipole is equal to zero due to mutual cancellation of the two summands in eq 5. As we show below, the passing of the adiabatic transition dipole of LIF through zero as a function of internuclear separation follows from the quantum mechanical calculations by Werner and Meyer.[21a] This result indicates that $|m_0^{12}|$ and $|\Delta m_0 V_{12}/\Delta I|$ ($|V_{12}/\Delta I| \ll 1$) can indeed be close in magnitude in real charge-transfer systems.

2.3. Radiative Rate and Transition Dipole. The influence of the solvent field results in the renormalization of the ET matrix element. Most experimental information about this parameter is extracted nowadays from transition moments of optical spectral lines. We therefore need to understand how the solvent effects discussed above influence the observed transition dipoles. We address this point here limiting our consideration to the two-state solute model.

Since the landmark work of Mulliken,[10] the radiative lifetimes of emission states[34] and oscillator strengths of absorption transitions[14] in charge transfer (CT) complexes are described in terms of the adiabatic transition dipole $\mathbf{M}_0^{12}$ (eq 5, see also eq A3 in the appendix). Below we will improve upon the classical results of the theory of spontaneous radiation rates in vacuum by explicitely taking into account fluctuations of the transition moment caused by the solvent thermal motions. The main component of this derivation is the two-step renormalization of the vacuum adiabatic transition dipole. Following the procedure outlined in section 2.1, as the first step, we will define the instantaneous transition dipole $\mathbf{M}^{12}$ equilibrated to the electronic subsystem of the solvent, but fluctuating with nuclear solvent configurations. Next, we will average the transition probability over the nuclear solvent fluctuations. The radiative rate constant (eq 34) is then expressed through the average $\langle\mathbf{M}^{12}\rangle_2$ of the instantaneous dipole $\mathbf{M}^{12}$ over the equilibrium configuration of the solvent corresponding to the solute excited state ($i = 2$).

The definition of the instantaneous transition dipole $\mathbf{M}^{12}$ is straightforward in terms of the procedure outlined in section 2.1. A canonical transformation of the system Hamiltonian $H_{\mathrm{R}} = \exp[iL]\, H \exp[-iL]$ changes the basis of harmonic oscillators representing the solvent electronic polarization to a coherent state of displaced harmonic oscillators. The average of the system density matrix $\exp[-\beta H_{\mathrm{R}}]$ over the solvent electronic subsystem yields the adiabatic ground state E^{e} (eq 11) built on diabatic states E_i (eq 13) and the renormalized ET matrix element $\tilde{V}_{12}$ (eqs 15 and 16). The diagonalization of the two-state Hamiltonian composed of E_i as diagonal elements and $\tilde{V}_{12}$ as off-diagonal elements gives the instantaneous adiabatic transition dipole

$$\mathbf{M}^{12} = \exp(-{}^{1}/{}_{2}S_{\mathrm{e}})\left[\mathbf{m}_0^{12}\frac{\Delta E}{\Delta\tilde{E}} - \Delta\mathbf{m}_0\frac{V_{12}^{\mathrm{eff}}}{\Delta\tilde{E}}\right] \qquad (25)$$

where $\Delta\tilde{E}$ is given by eq 12. $\mathbf{M}^{12}$ depends on the instantaneous nuclear configuration of the solvent through the inertial field

$\mathbb{E}_p$ entering $\Delta\tilde{E}$, ΔE, and V_{12}^{eff} according to eqs 12, 13, and 15, respectively.

Once we have the instantaneous adiabatic transition dipole, we need to determine an observable quantity (ensemble average) involving $\mathbf{M}^{12}$. The quantity usually available from experiment and directly connected to the magnitude of the adiabatic transition dipole is the rate of spontaneous emission k_{rad} that can be written as[34]

$$k_{\text{rad}} = \int k_{\text{rad}}(\bar{\nu})\mathrm{d}\bar{\nu} \tag{26}$$

where

$$k_{\text{rad}}(\bar{\nu}) = \frac{64\pi^4 f(\epsilon_\infty)c}{3}\bar{\nu}^3\langle|\mathbf{M}^{12}|^2\,\delta(hc\bar{\nu} - \Delta\tilde{E})\rangle_{2,v} \tag{27}$$

In eq 27, $\bar{\nu}$ is the wavenumber (in cm^{-1}), $\langle ...\rangle_{2,v}$ denotes an ensemble average over the vibrational excitations of the solute (v) and over the fluctuations of the inertial field ($\mathbb{E}_p$ (eq 18)) with the solute in the excited ($i = 2$) state. $f(\epsilon_\infty)$ in eq 27 is a function of the high-frequency dielectric constant ϵ_∞ of the solvent. In the classical Strickler–Berg theory,[35] $f(\epsilon_\infty) = \epsilon_\infty^{3/2}$. When the vacuum electric field of incident light is replaced by the local Lorentz field of the induced solvent dipoles, one obtains $f(\epsilon_\infty) = \sqrt{\epsilon_\infty}[(\epsilon_\infty + 2)/3]^2$.[36] Since other forms of $f(\epsilon_\infty)$ are also used in the literature,[37] we will not specify $f(\epsilon_\infty)$ in the derivation below.

From eqs 26 and 27 we have

$$k_{\text{rad}} = \frac{64\pi^4 f(\epsilon_\infty)}{3h^4c^3}\langle|\mathbf{M}^{12}|^2(\Delta\tilde{E}\ )^3\rangle_{2,v} \tag{28}$$

The average over $\mathbb{E}_p$ in eq 28 can be taken exactly if we replace $\Delta\tilde{E}$ by ΔE, which is a very good approximation for most optical chromophores. This yields

$$\langle|\mathbf{M}^{12}|^2(\Delta E)^3\rangle_2 = e^{-S_e}\Delta F_i[\mathbf{m}_0^{12}\Delta F_i - \mathbf{\Delta m}_0\langle V_{12}^{\text{eff}}\rangle_2]^2 + \{\text{terms proportional to } k_BT\}$$

The second summand ($\propto k_BT$) is of the order $1/\beta\Delta F_i$ of the first one. For usual magnitudes of optical energy gaps ΔF_i amounting to several electron volts we can neglect the terms proportional to k_BT and write

$$k_{\text{rad}} = \frac{32\pi^3 f(\epsilon_\infty)}{3\hbar}e^{-S_e}\langle\bar{\nu}_2[\mathbf{m}_0^{12}\bar{\nu}_2 - \mathbf{\Delta m}_0\langle V_{12}^{\text{eff}}\rangle_2/hc]^2\rangle_v \tag{29}$$

Here $\langle V_{12}^{\text{eff}}\rangle_2$ is the ET matrix element corresponding to the solvent configuration in equilibrium with the excited solute state. For arbitrary orientations of the ground and excited solute dipole moments we have

$$\langle V_{12}^{\text{eff}}\rangle_i = V_{12} - 2\mu_e(\mathbf{m}_0^{12}\cdot\bar{\mathbf{m}}_0) - 2\mu_p(\mathbf{m}_0^{12}\cdot\mathbf{m}_{0i}) \tag{30}$$

The two solvation terms in this equation are connected to the optical spectral shift $\Delta\bar{\nu}_i^p$ due to induction and dipolar solvation when both $\mathbf{m}_{01}$ and $\mathbf{m}_{02}$ are collinear and hence are oriented along $\mathbf{z}$

$$\langle V_{12}^{\text{eff}}\rangle_i = V_{12} + \frac{(\mathbf{m}_0^{12}\cdot\hat{\mathbf{z}})}{\Delta m_0}\,hc\Delta\bar{\nu}_i^p \tag{31}$$

The averaging over the vibronic envelope of the emission band in eq 29 can be performed in terms of a single high-frequency skeletal mode[32] or using the vibronic profile of the emission band obtained from experiment. The latter approach was used in the Strickler–Berg theory[35] and, following their arguments, we come to the final expression for the radiative rate constant

$$k_{\text{rad}} = \frac{32\pi^3 f(\epsilon_\infty)}{3\hbar}\Bigg[(m_0^{12})^2\langle\bar{\nu}_2^3\rangle_{\text{av}} - 2(\mathbf{m}_0^{12}\cdot\mathbf{\Delta m}_0)\langle\bar{\nu}_2^2\rangle_{\text{av}}\frac{\langle\tilde{V}_{12}\rangle_2}{hc} + \Delta m_0^2\langle\bar{\nu}_2\rangle_{\text{av}}\left(\frac{\langle\tilde{V}_{12}\rangle_2}{hc}\right)^2\Bigg] \tag{32}$$

Here

$$\langle\bar{\nu}_2^n\rangle_{\text{av}} = \frac{\int\bar{\nu}^{n-3}I_f(\bar{\nu})\,\mathrm{d}\bar{\nu}}{\int\bar{\nu}^{-3}I_f(\bar{\nu})\,\mathrm{d}\bar{\nu}}$$

and $I_f(\bar{\nu})$ is the intensity of the fluorescence spectrum (in terms of relative numbers of quanta at each frequency). If we neglect the effect of redistribution of electronic density between the two ET states on the transition dipole and put $\langle V_{12}\rangle_2 = 0$ in eq 32, we obtain the analogue of the radiative rate constant in the Strickler–Berg theory[35]

$$k_{\text{rad}}(\bar{\nu}) = \frac{32\pi^3 f(\epsilon_\infty)}{3\hbar}\langle\bar{\nu}_2^3\rangle_{\text{av}}(m_0^{12})^2 \tag{33}$$

which contains only the average frequency $\langle\bar{\nu}_2^3\rangle_{\text{av}}$. The majority of experimental emission rate data are treated according to eq 33 and only $\langle\bar{\nu}_2^3\rangle_{\text{av}}$ is commonly available. Therefore, for the theory–experiment comparison a simplification of the general expression 32 is desirable. This is achieved by analogy with eq 33

$$k_{\text{rad}} = \frac{32\pi^3 f(\epsilon_\infty)}{3\hbar}\langle\bar{\nu}_2^3\rangle_{\text{av}}|\langle\mathbf{M}^{12}\rangle_2|^2 \tag{34}$$

in terms of the adiabatic transition dipole at the equilibrium solvent configuration

$$\langle\mathbf{M}^{12}\rangle_i = \exp(-{}^1\!/_2S_e)\left[\mathbf{m}_0^{12} - \mathbf{\Delta m}_0\,\frac{\langle V_{12}^{\text{eff}}\rangle_i}{hc\bar{\nu}_i}\right] \tag{35}$$

We denote the projections of $\langle\mathbf{M}^{12}\rangle_i$ on the direction $\hat{\mathbf{z}}$ of the differential solute dipole and that perpendicular to it $\hat{\mathbf{x}}$ as longitudinal, $(M_i^{12})_{||}$, and transverse, $(M^{12})_\perp$, components ($\hat{\mathbf{z}}$ and $\hat{\mathbf{x}}$ are defined after eq 23). The equilibrium transition moment 35 can be obtained from eq 30 for arbitrary orientations of the solute dipole moments in the ground and excited states. Since the equation is rather cumbersome, we give here the transition dipole only for collinear $\mathbf{m}_{0i}$. In this case, eqs 31 and 35 yield[38]

$$(M^{12})_\perp = \exp(-{}^1\!/_2S_e)\ (\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) \tag{36}$$

$$hc\bar{\nu}_i(M_i^{12})_{||} = \exp(-{}^1\!/_2S_e)\ [(\mathbf{m}_0^{12}\cdot\hat{\mathbf{z}})(\Delta I + \Delta E^{\text{disp}}) - \Delta m_0V_{12}]$$

and

$$[\bar{\nu}_i\langle M^{12}\rangle_i]^2 = e^{-S_e}\ (\bar{\nu}_i^2(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}})^2 + [(\mathbf{m}_0^{12}\cdot\hat{\mathbf{z}})(\bar{\nu}_0 + \Delta\bar{\nu}^{\text{disp}}) - \Delta m_0V_{12}/hc]^2) \tag{37}$$

Equation 35 suggests that, because of unequal transition energies and equilibrium ET matrix elements for absorption and emission, adiabatic transition moments are also unequal, $\langle M^{12}\rangle_1$

$\neq \langle M^{12}\rangle_2$. This is in contrast to the conjugate relation $M_0^{12} = (M_0^{21})^*$ for the corresponding vacuum values. Note also that from eq 36 the following inequalities hold

$$\langle M^{12}\rangle_2 > \langle M^{12}\rangle_1$$

for positively solvatochromic dyes with $m_{02} > m_{01}$, $\bar{\nu}_2 < \bar{\nu}_1$ and

$$\langle M^{12}\rangle_2 < \langle M^{12}\rangle_1$$

for transitions with $m_{02} < m_{01}$, $\bar{\nu}_2 > \bar{\nu}_1$.

Expressions 36 and 37 are the major results of the derivation in this section. From eq 36 we learn that the product of the longitudinal projection $(M_i^{12})_{\|}$ on the average transition frequency $\bar{\nu}_i$ depends on the solvent only through the differential dispersion term ΔE^{disp}. Since ΔE^{disp} is not directly related to solvent polarity, a dependence of $\bar{\nu}_i\langle M^{12}\rangle_i$ on solvent dipolar strength, if it exists, is caused by a nonzero transverse projection $(M^{12})_\perp$. The latter can be found when transition dipoles are known for both absorption and emission, since

$$\begin{aligned}[\bar{\nu}_1\langle M^{12}\rangle_1]^2 - [\bar{\nu}_2\langle M^{12}\rangle_2]^2 &= e^{-S_e}(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}})^2(\bar{\nu}_1^2 - \bar{\nu}_2^2) \\ &\cong 2(M^{12})_\perp^2\bar{\nu}_0\Delta\bar{\nu}_{\text{st}} \qquad (38)\end{aligned}$$

where $\Delta\bar{\nu}_{\text{st}}$ is the Stokes shift and the assumption $|\bar{\nu}_i - \bar{\nu}_0| \ll \bar{\nu}_0$ is used in the second line in eq 38. Since the oscillator strength F_i^{12} is related to the transition moment

$$F_i^{12} = 0.47 \times 10^{-6}\bar{\nu}_i\langle M^{12}\rangle_i^2$$

($\bar{\nu}_i$ is in cm^{-1} and $\langle M^{12}\rangle_i$ is in debyes), the corresponding modification of eq 38 in terms of oscillator strengths is straightforward.

3. Discussion

Our description of the solvent effect on ET kinetics and optical transitions in condensed phases is based on the Hamiltonian 4. In the framework of this model, the fluctuations of the diabatic electronic levels are controlled by the interaction of the diabatic solute dipole moments $\mathbf{m}_{0i}$ (diagonal matrix elements of the electric dipole operator) with the total (inertial + inertialess) field of the solvent. By the same token, the fluctuations of the ET matrix element are controlled by the interaction of the diabatic transition dipole $\mathbf{m}_0^{12}$ (off-diagonal matrix element of the electric dipole operator) with the same solvent field. The adiabatic exclusion of the inertialess electronic subsystem (according to eq 1) results in instantaneous free energies and also renormalizes the ET matrix element. The instantaneous free energies and the renormalized matrix element both include two similar components: equilibrium solvation by bound solvent electrons and nonequilibrium solvation by the nuclear subsystem (cf. eqs 13 and 15). There is thus a significant self-consistency between the diagonal and off-diagonal elements of the effective two-state “Hamiltonian”[39] built on E_i and $\tilde{V}_{12}$.

Instantaneous free energies and the renormalized ET matrix element (eqs 13, 15, and 16) are then used to calculate the ET rate constant (section 2.2), radiative rates (section 2.3), and to get absorption intensities (section 3.2 below). The major difference between our results presented in sections 2.2 and 2.3 and those from classical studies on nonadiabatic ET and CT spectra[7,11−14] is the new expressions for the rate constant preexponent (eq 21) and the adiabatic transition dipole (eq 35). The origin of the difference is the renormalization of the ET matrix element which has not been accounted for in previous studies. The key parameters of the renormalization are the orientation (relative to the differential solute dipole moment) and the magnitude of the diabatic transition dipole $\mathbf{m}_0^{12}$ which we discuss next.

3.1. Diabatic Transition Dipole and ET Rate. The diabatic transition dipole $\mathbf{m}_0^{12}$ is commonly neglected in the theories of ET[7] and spectroscopy of CT complexes.[11−14,34] It is assumed that optical CT transitions occur due to the adiabatic transition dipole

$$\langle \mathbf{M}_{\text{MH}}^{12}\rangle_i = -\Delta\mathbf{m}_0\frac{V_{12}}{hc\bar{\nu}_i} \qquad (39)$$

that depends on the solvent only through the vertical transition energy $hc\bar{\nu}_i$. Approximation 39 goes back to Mulliken (CT spectra),[10] Hush (intervalence transitions),[11] and Hopfield.[12] The most thorough analysis of the accuracy of eq 39 belongs perhaps to Mulliken,[10] although Hopfield estimated the error of neglecting of $\mathbf{m}_0^{12}$ amounting to 25% for long-range ET in biological systems.[12a] According to Mulliken (ref 10, chapter 3.4), the omission of the diabatic transition dipole can be justified only for strong donor-acceptor complexes (large $|V_{12}|$). For weak complexes, $\mathbf{m}_0^{12}$ “might be large enough to give some considerable intensity to the CT band”[10] even when the charge redistribution term $|V_{12}\Delta\text{m}_0/hc\bar{\nu}_i|$ results in very little intensity. The nonzero value of $\mathbf{m}_0^{12}$ “may well often explain the rather considerable intensities of CT absorption bands for weak complexes”[10] and high rates of spontaneous emission (see below). It is therefore the case of weak coupling (small $|V_{12}|$), which is of major importance for ET applications, where, according to Mulliken, $\mathbf{m}_0^{12}$ should be a substantial component of the adiabatic transition dipole (eq 5). Quantum mechanical electronic structure calculations are needed to accurately determine the magnitude of $\mathbf{m}_0^{12}$. Here we present only some crude estimates.

The relative magnitudes of the two summands in the adiabatic transition dipole given by eq 5 can be estimated from the Mulliken approximation[40] saying that for an arbitrary quantum operator $\hat{A}$ its off-diagonal matrix element is expressed through the mean of the diagonal elements as follows

$$\langle\phi_1|\hat{A}|\phi_2\rangle = (\langle\phi_1|\phi_2\rangle/2)(\langle\phi_1|\hat{A}|\phi_1\rangle + \langle\phi_2|\hat{A}|\phi_2\rangle) \qquad (40)$$

This relation predicts that $\mathbf{m}_0^{12}$ is directed as the vector $\mathbf{m}_{01} + \mathbf{m}_{02}$ and we get

$$\left|\frac{(\mathbf{m}_0^{12}\cdot\hat{\mathbf{z}})\,\Delta I}{V_{12}\Delta m_0}\right| = \left|\frac{\Delta I}{I_1 + I_2}\frac{m_{02}^2 - m_{01}^2}{(\Delta m_0)^2}\right| \qquad (41)$$

and

$$\left|\frac{(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}})\,\Delta I}{V_{12}\Delta m_0}\right| = \left|\frac{\Delta I}{I_1 + I_2}\frac{2m_{01}m_{02}\sin\varphi}{(\Delta m_0)^2}\right| \qquad (42)$$

where φ is the angle between $\mathbf{m}_{01}$ and $\mathbf{m}_{02}$. From eq 41 we come directly to the parameter θ of eq 22

$$\theta_{\mathrm{M}} = 1 - \frac{\Delta I + \Delta E^{\mathrm{disp}}}{I_1 + I_2}\frac{m_{02}^2 - m_{01}^2}{(\Delta m_0)^2} - \frac{4m_{02}^2\, m_{01}^2 \sin\varphi}{(\Delta m_0)^2 (I_1 + I_2)}(\mu_{\mathrm{p}} + \mu_{\mathrm{e}}) \quad (43)$$

where the subscript "M" stands for the Mulliken approximation.

In the Mulliken scheme, I_i are the energies of two localized electronic states measured from the ionization limit ($I_i = -\mathrm{PI}_i$, where PI_1 and PI_2 are the ionization potentials of D and A^-, respectively, in the donor−acceptor complex D−A).[40b] The Mulliken approximation hence predicts that the contribution of the direct overlap, m_0^{12}, to the adiabatic transition dipole M_0^{12} decreases compared to the charge redistribution component, $V_{12}\Delta m_0/\Delta I$, with deepening the electronic levels of the donor and acceptor moieties. Similarly, deepening of the donor and acceptor electronic levels decreases the impact of solvation on the tunneling probability leading, in the limit $|I_1/\Delta I| \rightarrow \infty$, to the standard eq 20 for the rate constant preexponent. A physically similar picture follows from the Redi−Hopfield model[12b] where the dependence of the electronic coupling on the energy of the localized state has been taken into account. The difference between optical and thermal ET matrix elements is scaled as $|\Delta I/I_1|$ in the Redi−Hopfield theory analogously to our result 43.

It is interesting to estimate the impact of different terms in adiabatic transition dipole (eq 5) and the rate constant preexponent (eq 21). We do it here for the coumarin-153 (C153) dye as an example. For C153, we have $m_{01} = 6.55$ D, $m_{02} \cong 15$ D,[41a] $\varphi = 10.4°$,[41b] $I_1 = -8.5$ eV, and $I_2 = -5.2$ eV.[41c] The ratios 41 and 42 are equal to, respectively, 0.60 and 0.12. In order to get the Franck−Condon factor S_{e} and the transverse solvation terms (the last summand in eq 43 and the second term in the brackets in eq 21) we need the response functions μ_{p} and μ_{e}. We estimate them from the dielectric continuum relations 8 and 9 with $R_0 = 4$ Å, $\epsilon_{\mathrm{s}} = 30$, and $\epsilon_\infty = 2$. With $\hbar\omega_{\mathrm{s}} = 5$ eV this gives $S_{\mathrm{e}} = 0.03$. The term in the brackets in eq 21 reads in the Mulliken approximation as

$$|V_{12}\theta_i|^2 + 2\beta^{-1}\,\mu_{\mathrm{p}}|(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}})|^2 = |V_{12}|^2\left[\theta_{\mathrm{M}}^2 + 2\beta^{-1}\,\mu_{\mathrm{p}}\left|\frac{2m_{01}m_{02}\sin\varphi}{(I_1 + I_2)\Delta m_0}\right|^2\right]$$

The second summand here is equal to 2×10^{-5} for C153 and the last summand in eq 43 amounts to 8×10^{-3}. Both are negligible compared to other contributions, and for the parameter θ_{M} we have ($\Delta E^{\mathrm{disp}} \simeq 0$) $\theta_{\mathrm{M}} = 1.6$. Also, since the ratio 42 is small, the adiabatic transition dipole obtained from the exact relation 5 is given by the product of θ and the adiabatic transition dipole in the Mulliken−Hush approximation

$$M_0^{12} \cong \theta M_{\mathrm{MH}}^{12}$$

where M_{MH}^{12} refers to the vacuum transition dipole in eq 39 with $hc\bar{\nu}_i = \Delta J$. The estimates performed here enable us to draw several important conclusions: (i) the Franck−Condon factor S_{e} and the second term in brackets in eq 21 are both small and can be omitted, (ii) the ET rate constant differs substantially (2.6 times higher for C153) from the traditional golden-rule expressions 19 and 20, (iii) the diabatic transition dipole makes a significant contribution to the adiabatic transition dipole (eq 5) that is θ times higher ($\theta_{\mathrm{M}} = 1.6$ for C153) than in the Mulliken−Hush approximation (eq 39). We can thus simplify the equation for the rate constant preexponent as follows

$$A = \theta^2 A_{\mathrm{NA}}$$

where θ is given by eq 23. Note also that in C153 the optical transition occurs from the deep ground S_0 state. Many ET systems are experimentally prepared by photoexcitation of either donor or acceptor moieties.[13b,34,42] In those cases, the portion of $\mathbf{m}_0^{12}$ in the adiabatic transition dipole is expected to be even more substantial.

A procedure called a generalized Mulliken−Hush approach has been recently proposed by Cave and Newton[21b,c] to overcome the difficulty of nonzero $\mathbf{m}_0^{12}$ and to provide an unambiguous connection between adiabatic and nonadiabatic parameters (see the Appendix). The procedure utilizes a transformation of the diabatic basis $\{\phi_1, \phi_2\} \rightarrow \{\phi_a, \phi_b\}$ (explicitly given by eqs A6 and A7) that diagonalizes the dipole moment matrix. In the basis $\{\phi_a, \phi_b\}$, the two-state Hamiltonian 4 transforms to

$$\tilde{H}_0 = \sum_{i=a,b}(I_i - \mathbf{m}_{0i}\cdot(\mathbb{E}_{\mathrm{p}} + \mathbb{E}_{\mathrm{e}}))\, b_i^+ b_i + (V_{ab} - \mathbf{m}_0^{ab}\cdot(\mathbb{E}_{\mathrm{p}} + \mathbb{E}_{\mathrm{e}}))\,(b_1^+ b_2 + b_2^+ b_1) \quad (44)$$

where b_i^+ and b_i now denote the creation and annihilation operators in the diabatic states a and b with the energies I_a (eq A8) and I_b (eq A9) specified in the appendix. The off-diagonal matrix element $\mathbf{m}_0^{ab}$ reads

$$\mathbf{m}_0^{ab} = \mathbf{m}_0^{12}\frac{\Delta m_0}{\Delta M_{12}} - \Delta\mathbf{m}_0\frac{m_0^{12}}{\Delta M_{12}}$$

where

$$\Delta M_{12}^2 = \Delta M^2 + 4(M_0^{12})^2 = \Delta m_0^2 + 4(m_0^{12})^2 \qquad (45)$$

and ΔM is given by eq A4 in the Appendix. When $(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) = 0$, $\mathbf{m}_0^{ab}$ is identically zero and the adiabatic transition dipole

$$M_0^{12} = \Delta M_{12}\frac{V_{ab}}{\Delta J}$$

is directly connected to the ET matrix element

$$V_{ab} = V_{12}\frac{\Delta m_0}{\Delta M_{12}} - \Delta I\frac{m_0^{12}}{\Delta M_{12}} \qquad (46)$$

The advantage of using the transformation $\{\phi_1,\phi_2\} \rightarrow \{\phi_a,\phi_b\}$ is that it makes exact the Mulliken−Hush connection between the transition dipole and the ET matrix element and yields diabatic quantities slowly varying with nuclear coordinates.[21a] However, for the complete description of the ET problem, we need the nonadiabatic rate constant derived through the perturbation expansion in terms of the hopping Hamiltonian in eq 44. The derivation is the same as that carried out in section 2.2. It even simplifies when the transition dipole $\mathbf{m}_0^{ab}$ is zero. Since the hopping Hamiltonian does not depend on the solvent field in this case, the preexponential factor of the rate constant is given by the usual expression 20 with V_{12} replaced by V_{ab}. The cost of preserving the simple connection to the transition dipole and the traditional form of the rate constant preexponent is the complicated form of the activation barrier which now loses the appealing physical clarity it had in the basis $\{\phi_1, \phi_2\}$. The vertical energy gap ΔF_i entering the activation barrier in eq 19 becomes

$$\Delta F_i = \Delta I \frac{\Delta m_0}{\Delta M_{12}} + 2V_{12}\frac{m_0^{12}}{\Delta M_{12}} - (\mu_{\mathrm{e}} + \mu_{\mathrm{p}})\Delta M_{12}(m_{01} + m_{02}) \pm \lambda_{\mathrm{p}}$$

with

$$\lambda_{\mathrm{p}} = \mu_{\mathrm{p}}[\Delta m_0^2 + 4(m_0^{12})^2]$$

The solvent reorganization energy is no longer the solvation energy of the differential solute dipole by inertial solvent modes and involves now the transition dipole. Also induction forces (proportional to m_{0i}^2) and dispersion interactions (given in terms of m_0^{12}) are now entangled in a nontrivial way in the vertical energy gap. The two descriptions in terms of Hamiltonians H_0 and $\tilde{H}_0$ might be equivalent mathematically (within the range of applicability of the perturbation expansion different for the two Hamiltonians). We however prefer that in terms of the Hamiltonian H_0, since it preserves the representation of the ET energetics in terms of fundamental interaction potentials: inductions, dispersions, and dipolar interactions. There is obviously nothing fundamental in the particular form 20 of the rate constant preexponential factor and we sacrifice it in favor of the physical clarity of the barrier thermodynamics. In fact, as we see below, the Mulliken−Hush connection between the transition dipole and ET matrix element remains exact when the effective matrix element H_{DA} instead of V_{12} is used and, in turn, H_{DA} has a simple connection to V_{ab}.

Before proceeding to the analysis of transition dipoles we first summarize our findings concerning nonradiative transitions: (1) The renormalization of the ET matrix element by the equilibrium field of solvent electrons and the instantaneous field of the nuclear subsystem result in a new form of the preexponential factor of the nonadiabatic ET rate constant (eq 21). (2) The deviation of the new preexponent from the well-known expression 20 is controlled by the magnitude and orientation of the diabatic transition dipole $\mathbf{m}_0^{12}$ relative to the differential solute dipole $\Delta\boldsymbol{m}_0$. (3) When the projection of $\mathbf{m}_0^{12}$ transverse to $\Delta\mathbf{m}_0$ and the parameter θ (eq 23) are both zero, the transferred electron is localized at the donor or acceptor sites, since the ET rate constant is zero. The transverse solvation term (the second summand in brackets in eq 21) is small and the ET rate is substantially diminished when only $\theta = 0$.

3.2. Transition Moments from Emission Lifetimes. In the two-state Mulliken−Hush formula (eq 39), the transition dipole is inversely proportional to the transition frequency and k_{rad} is approximately (neglecting the difference between $\langle\bar{\nu}_2^3\rangle_{\mathrm{av}}$ and $\langle\bar{\nu}_2\rangle_{\mathrm{av}}^3$) linear in $\bar{\nu}_2$ (substitute eq 39 into eq 34). Several observations proved to conflict with the two-state Mulliken−Hush picture: (i) plots of k_{rad} vs $\bar{\nu}_2$ are often curved,[34a,b] (ii) products of transition dipoles from eq 34 and corresponding transition frequencies may depend on the solvent,[43] and (iii) ET matrix elements obtained by combining eqs 34 and 39 are sometimes unphysically high.[44]

Two explanations of the disagreement between the Mulliken−Hush theory and experiment have been proposed in the literature. As we have alluded to above, the Mulliken explanation was that it is m_0^{12} that is nonnegligible and eq 5 instead of eq 39 should be used. Murrell[10,45] advanced an alternative mechanism of "intensity borrowing" due to coupling of the CT states to a localized excited state of either donor or acceptor. In the Murrell scheme, both the solvent dependence of $\langle M^{12}\rangle_2\bar{\nu}_2$ and curved k_{rad} vs $\bar{\nu}_2$ were attributed to the change of the strength of coupling to locally excited states caused by the variation of the vertical energy gap $\bar{\nu}_2$. Eventually, the Murrell scheme became prevailing in treating transition dipoles,[34a,b,43b,c,46] although no detailed studies of the effect of m_0^{12} have been conducted. Here we try to analyze the Mulliken and Murrell concepts in the framework of our derivation in section 2.3.

Our basic results concerning the solvent and transition energy dependences of the transition dipole are given by eqs 36 and 37. From eq 37 we get

$$\bar{\nu}_2^3(\langle M^{12}\rangle_2)^2 = \bar{\nu}_2^3(M^{12})_{\perp}^{2} + \bar{\nu}_2(M_2^{12})_{\parallel}^{2}$$

This means that any curvature of the k_{rad} vs $\bar{\nu}_2$ plot is produced in the two-state model by the transverse component $(M^{12})_{\perp}$. In CT complexes with long-distance charge relocalization $\mathbf{m}_0^{12}$ is expected to be directed along $\Delta\boldsymbol{m}_0$[47] and the transverse component should be small. Therefore, even for nonzero m_0^{12}, the condition $(M^{12})_{\perp} = 0$ implies that the Mulliken−Hush dependence $k_{\mathrm{rad}} \propto \bar{\nu}_2$ must hold. The naive expectation that the linear trend $k_{\mathrm{rad}} \propto \bar{\nu}_2$ should break down when $\langle M^{12}\rangle_2 \cong m_0^{12} - \Delta m_0 V_{12}/hc\bar{\nu}_2$ is substituted into eq 34 is therefore incorrect. The reason is the dependence of the effective ET matrix element on the solvent equilibrium field. The spectral shift due to the solvent permanent dipoles and induction forces cancels out in the equilibrium transition dipole given in eq 35 and the product of its longitudinal component and the transition frequency varies with solvent only through the dispersion shift ΔE^{disp} (eq 36). ΔE^{disp} does not directly correlate with solvent polarity, and therefore, ΔE^{disp} is not expected to result in any particular variation of the transition dipole with increasing dipolar strength of the solvent. For $|\Delta E^{\mathrm{disp}}/\Delta I| \ll 1$ the solvent dependence vanishes altogether.

We can thus draw two important qualitative conclusions valid for the two-state solute with $(M^{12})_{\perp} = 0$: (i) the radiative rate constant is proportional to the transition energy and (ii) the product of the transition dipole and the transition frequency is invariant of the solvent. Consequently, a nonlinear dependence of k_{rad} on $\bar{\nu}_2$ and/or a noticeable variation of $\bar{\nu}_2\langle M^{12}\rangle_2$ with solvent indicates that the Murrell mechanism of "intensity borrowing" is in order. In fact, for all the data on transition dipoles in different solvents we found in the literature,[34b,43] there is a pronounced (and usually linear) dependence of $\bar{\nu}_2\langle M^{12}\rangle_2$ on the transition frequency. This may indicate that in real systems the effect on transition dipoles of mixing of CT states with localized excited states is substantial or even dominant.[34a]

We however need to stress that both manifestations of the Murrell intensity borrowing mechanism, curvature of k_{rad} vs $\bar{\nu}_2$ and the solvent dependence of $\bar{\nu}_2\langle M^{12}\rangle_2$, also follow from a nonzero $(M^{12})_{\perp}$ component. For most ET systems the Franck−Condon factor S_{e} of electronic polarizability is very small and eq 37 predicts a linear variation of $(\bar{\nu}_2\langle M^{12}\rangle_2)^2$ with $\bar{\nu}_2^2$. In Figure 1 we plotted this dependence using recent experimental data of Kapturkiewicz and Herbich.[43c] A fairly good linear correlation is actually seen. Moreover, the plot of $[\bar{\nu}_1\langle M^{12}\rangle_1]^2 - [\bar{V}_2\langle M^2\rangle_2]^2$ vs $(\bar{\nu}_1^2 - \bar{\nu}_2^2)$ shown in the lower part in Figure 1 is linear too, in accord with eq 38. Nevertheless, a coupling to excited states might produce the same types of correlations and it seems impossible to distinguish between the two mechanisms without additional data. The information lacking in all measurements of the solvent dependence of transition dipoles is the

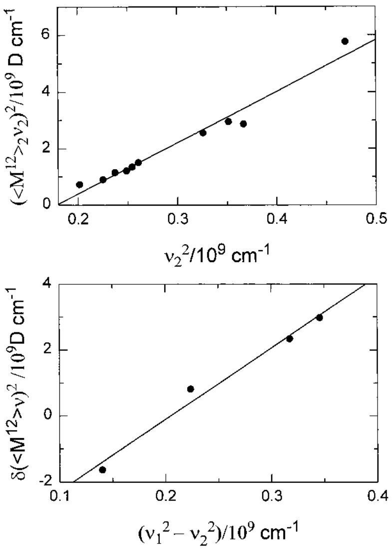

Figure 1. Solvent polarity dependence of the transition moment according to the data by Kapturkiewicz and Herbich.[43c] The upper panel corresponds to emission data in different solvents (points). The lower part gives the difference $\delta(\langle M^{12}\rangle\bar{\nu})^2 = (\langle M^{12}\rangle_1\bar{\nu}_1)^2 - (\langle M^{12}\rangle_2\bar{\nu}_2)^2$ vs the difference of squared wavenumbers for absorption and emission. The solid lines represent regressions drawn through the experimental points.

angle between $\mathbf{m}_0^{12}$ and $\Delta\mathbf{m}_0$ (or, at least, $(M^{12})_\perp$). Knowledge of the relative orientation of the two vectors would enable one to discriminate between the Murrell mechanism and the two-state formulation by using eqs 36−37.

The analysis of radiative lifetimes yields adiabatic CT transition dipoles. It does not, however, provide a procedure for splitting the moment $\langle M^{12}\rangle_1$ into its m_0^{12} and $(\langle V_{12}^{\mathrm{eff}}\rangle_2/hc\bar{\nu}_2)\Delta m_0$ components, according to eq 35. However, for nonadiabatic ET, we actually do not need V_{12} itself. Indeed, for $(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) = 0$, only the product $V_{12}\theta$ and not V_{12} alone enters the rate constant preexponent as the ET matrix element (eq 21). In fact for $(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) = 0$ we can recover the traditional form of the nonadiabatic rate constant (eqs 19 and 20) just by replacing V_{12} in eq 20 by the effective condensed phase value

$$|H_{\mathrm{DA}}| = \exp(-{}^1/_2S_{\mathrm{e}})|V_{12}\theta| = \exp(-{}^1/_2S_{\mathrm{e}})\left|\frac{m_0^{12}}{\Delta m_0}(\Delta I + \Delta E^{\mathrm{disp}}) - V_{12}\right| \quad (47)$$

This ET matrix element is connected to the longitudinal projection of the condensed phase transition dipole by the expression

$$|H_{\mathrm{DA}}| = \frac{hc\bar{\nu}_i(M_i^{12})_{\|}}{\Delta m_0}$$

When $(M^{12})_\perp = (\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) = 0$, we have the formula

$$|H_{\mathrm{DA}}| = \frac{hc\bar{\nu}_i\langle M^{12}\rangle_i}{\Delta m_0} \quad (48)$$

recovering the Mulliken−Hush relation that now becomes exact. We therefore do not need to split $\langle M^{12}\rangle_i$ into the diabatic transition dipole m_0^{12} and the vacuum ET matrix element V_{12} parts and we can get the effective ET matrix element directly from the transition dipole according to eq 48.

When the dispersion component of the spectral shift ΔE^{disp} is small compared to ΔI, our treatment predicts that the product of the vacuum values of the transition frequency and transition dipole is related to the same product in the liquid as follows

$$\bar{\nu}_0 M_0^{12} = \exp(-{}^1/_2S_{\mathrm{e}})\,\bar{\nu}_i\langle M^{12}\rangle_i$$

Since S_{e} is usually much less then unity, eq 48 gives a simple recipe for calculating the transition dipole in condensed phases from its vacuum value

$$\langle M^{12}\rangle_i = M_0^{12}/(1 + \Delta\bar{\nu}_i/\nu_0), \quad \Delta\bar{\nu}_i = \bar{\nu}_i - \bar{\nu}_0$$

Also eq 48 can be rewritten as

$$|H_{\mathrm{DA}}| = \frac{hc\bar{\nu}_0 M_0^{12}}{\Delta m_0} \quad (49)$$

This is an important result indicating that the ET matrix element H_{DA} in condensed phases can be obtained from the vacuum adiabatic transition dipole and the vacuum transition frequency. To be precise, we list the assumptions underlying eq 49: (i) $\mathbf{m}_{01}$ is collinear with $\mathbf{m}_{02}$, (ii) $(\mathbf{m}_0^{12}\cdot\hat{\mathbf{x}}) = 0$, and (iii) $|\Delta E^{\mathrm{disp}}/\Delta I| \ll 1$. Equation 49 also implies that we can establish a simple relation between H_{DA} and the ET matrix element V_{ab} calculated by the method of Cave and Newton[21b,c] (eq 46)

$$|H_{\mathrm{DA}}| = \exp(-{}^1/_2S_{\mathrm{e}})\frac{\Delta M_{12}}{\Delta m_0}|V_{ab}| \quad (50)$$

H_{DA} is also connected to the extinction coefficient $\epsilon(\nu)$ for absorption. Since an exact expression for $\epsilon(\nu)$ is available in terms of our model, we present it here for completeness. $\epsilon(\nu)$ can be obtained by using the Einstein relations between the absorption and emission rates[35b] and $k_{\mathrm{rad}}(\bar{\nu})$ defined in eq 27. This yields

$$\frac{\epsilon(\nu)}{\nu} = \left(\frac{8\pi^3 N_{\mathrm{A}} f(\epsilon_\infty)}{3000\ \ln(10)c\epsilon_\infty}\right)|M(\nu)|^2$$

Here N_{A} is the Avogadro number and

$$|M(\nu)|^2 = \left[\Delta m_0^2\frac{|H_{\mathrm{DA}}|^2}{(h\nu)^2} + [(M^{12})_\perp]^2\,(1 + 2\lambda_{\mathrm{p}}/\beta(h\nu)^2)\right]\frac{\mathrm{FC}(\Delta F_1 - h\nu)}{(4\pi\lambda_{\mathrm{p}}k_{\mathrm{B}}T)^{1/2}}$$

where FC(ΔE) is given by eq 19 in our model and is easily generalized to include intramolecular quantum vibrations.[32,34b]

The effective ET matrix element H_{DA} is, according to eq 47, a complex function of both the electronic overlap (m_0^{12} and V_{12}) and the solvent (through ΔE^{disp}). Notice that H_{DA} and hence the rate constant preexponent depends on the vacuum energy gap ΔI. Since m_0^{12} and V_{12} also contain a generally unknown dependence on ΔI,[40b] we will not address this point here. As an illustration of the complicated nature of H_{DA}, we plotted in Figure 2 (upper part, curve 1) the dependence of H_{DA} on the interatomic distance in the LiF diatomic molecule in vacuum representing perhaps one of the simplest ET systems. H_{DA} is obtained according to eq 49 from the quantum-mechanical calculations by Werner and Meyer.[21a] The matrix element $|V_{ab}|$ that is also shown in Figure 2 (upper panel, curve 2) is slightly smaller than $|H_{\mathrm{DA}}|$ as expected from eqs 45 and 50. As is seen from Figure 2, only at large separations does H_{DA} decay exponentially with distance, as is usually assumed. At distances close to the equilibrium separation in the LiF

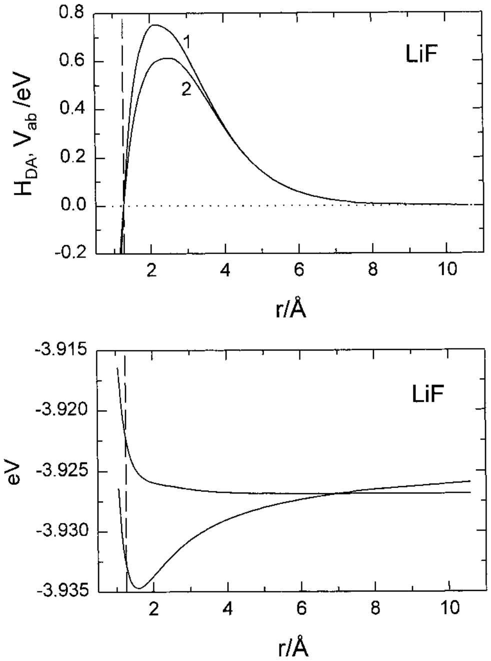

Figure 2. The effective ET matrix elements (1) $|H_{DA}|$ and (2) $|V_{ab}|$ vs the interatomic distance in the LiF diatomic molecule (upper panel). $|H_{DA}|$ is obtained according to eq 49 from the calculations by Werner and Meyer[21a] for the two lowest $^1\Sigma^+$ states of LiF shown in the lower panel. The dashed lines indicate the ET localization point.

molecule H_{DA} passes through a maximum and then goes through zero at a smaller distance. The latter behavior is a prediction of the present theory and the point $H_{DA} = 0$ corresponds to localization of the transferred electron. In the lower part in Figure 2 we give adiabatic electronic terms of the ground and excited states[21a] in order to show that in LiF localization occurs in the repulsive region of the intermolecular potential. We stress here again that localization happens only in the first order perturbation expansion for the rate constant. Higher order contributions

$$k_{NA} \propto \sum_{\alpha} |H_{A\alpha}|^2 |H_{\alpha D}|^2$$

may be nonzero, but the rate constant should be substantially diminished at $H_{DA} = 0$.

Finally, we comment on the dependence of the ET rate constant on the orientation of the diabatic transition dipole $\mathbf{m}_0^{12}$. It seems that the description developed in the present paper may be applicable to many CT systems. CT states are often created by optical excitation of the donor or acceptor moieties with a dipole moment of a photoexcited moiety oriented nonparallel to the direction of CT. In such cases, $\mathbf{m}_0^{12}$ and $\Delta\mathbf{m}_0$ are noncolinear leading to the type of solvent dependence of the adiabatic transition moment discussed above. Changing the orientation of $\mathbf{m}_0^{12}$ relative to $\Delta\mathbf{m}_0$ opens an additional degree of freedom influencing the ET rate. Some optical chromophores indeed show strong sensitivity of the orientation of their transition dipoles to conformations.[48] It might be interesting to look at the dependence of the transition moment orientation on the twisting angle in twisted ET systems where ET is suppressed at the out-off-plane orientation of the donor and acceptor subunits.[47b] Note also that rotation of $\mathbf{m}_0^{12}$ relative to $\Delta\mathbf{m}_0$ may be used in creating molecular switches.

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Appendix

Here we derive eq 5 for the transition moment in the adiabatic basis Ψ_1, Ψ_2 diagonalizing the vacuum two-state Hamiltonian. The basis Ψ_i is formed by the linear combination of the diabatic wavefunctions φ_i which, following Lu et al.,[49] we will write in terms of the CT fraction f

$$\Psi_1 = \sqrt{1-f}\varphi_1 - \mathrm{sign}(V_{12})\sqrt{f}\varphi_2 \qquad \text{(A1)}$$

$$\Psi_2 = \mathrm{sign}(V_{12})\sqrt{f}\varphi_1 + \sqrt{1-f}\varphi_2$$

where

$$f = \frac{1}{2} - \frac{\Delta I}{2\Delta J}, \quad \Delta J = \sqrt{\Delta I^2 + 4|V_{12}|^2} \qquad \text{(A2)}$$

and $\mathrm{sign}(V_{12})$ in eq A1 appears as a result of the convention $\sqrt{f(1-f)} = |V_{12}|/\Delta J$, $\Delta J > 0$. The adiabatic transition dipole

$$\mathbf{M}_0^{12} = \langle \Psi_1 | \hat{\mathbf{m}}_0 | \Psi_2 \rangle \qquad \text{(A3)}$$

is the off-diagonal matrix element of the electric dipole moment operator of the solute in the adiabatic basis A1. From eqs A1–A3 we get

$$\Delta\mathbf{M} = \mathbf{M}_0^{22} - \mathbf{M}_0^{11} = \Delta\mathbf{m}_0 \frac{\Delta I}{\Delta J} + \mathbf{m}_0^{12} \frac{4V_{12}}{\Delta J} \qquad \text{(A4)}$$

$$\mathbf{M}_0^{12} = \mathbf{m}_0^{12} \frac{\Delta I}{\Delta J} - \Delta\mathbf{m}_0 \frac{V_{12}}{\Delta J} \qquad \text{(A5)}$$

Equations A4 and A5 give the adiabatic differential and transition dipoles in terms of diabatic parameters. The problem usually appearing in quantum mechanical calculations is to get the inverse solution: to determine diabatic parameters from known adiabatic ones.[21] This task cannot be solved in the general case, because it demands determination of six diabatic parameters

$$I_1, I_2, V_{12}, m_{01}, m_{02}, m_0^{12}$$

from five adiabatic quantities

$$J_1, J_2, M_0^{11}, M_0^{22}, M_0^{12}$$

The trick used to overcome this difficulty is to reduce the number of diabatic dipole moments by using a linear transformation of the diabatic basis $\{\phi_1,\phi_2\} \rightarrow \{\phi_a,\phi_b\}$ diagonalizing the dipole moment matrix.[21] The transformation of the basis resulting in $\langle \phi_a | \hat{\mathbf{m}}_0 | \phi_b \rangle = 0$ can be explicitly written as follows ($m_0^{12} > 0$)

$$\phi_a = \sqrt{1-g}\phi_1 - \sqrt{g}\phi_2 \qquad \text{(A6)}$$

$$\phi_b = \sqrt{g}\phi_1 + \sqrt{1-g}\phi_2 \qquad \text{(A7)}$$

where

$$g = \frac{1}{2} - \frac{m_0^{12}}{\Delta M_{12}}$$

and ΔM_{12} is given by eq 45. In this basis, we have only five diabatic parameters that can be fully defined in terms of adiabatic state properties. The diabatic energies become

$$I_a = (1 - g)I_1 + gI_2 - (2m_0^{12}/\Delta M_{12})\, V_{12} \tag{A8}$$

$$I_b = gI_1 + (1 - g)I_2 + (2m_0^{12}/\Delta M_{12})\, V_{12} \tag{A9}$$

and the ET matrix element V_{ab} is given by eq 46.

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(39) The diabatic energies E_i and the renormalized ET matrix element form the effective Hamiltonian H_0^{eff} analogous to that in eq 4. The time-dependent perturbation theory applied to this Hamiltonian leads to the rate constant in eq 3. One should however be cautious using the term Hamiltonian for H_0^{eff}, since actually it is a partial free energy depending on temperature in the general case,[18] as follows from eq 1.

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