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Complete List of Authors:	Matyushov, Dmitry; Arizona State University, School of Molecular Sciences Newton, Marshall; Brookhaven National Laboratory, Chemistry

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Optical Absorption by Charge-Transfer Molecules

Dmitry V. Matyushov^{*,†} and Marshall D. Newton^{*,‡}

[†]*Department of Physics and School of Molecular Sciences, Arizona State University, PO Box 871504, Tempe, Arizona 85287*

[‡]*Brookhaven National Laboratory, Chemistry Department, Box 5000, Upton, NY 11973-5000, United States*

E-mail: dmitrym@asu.edu, Tel:(480)965-0057; newton@bnl.gov

Abstract

An analytical formalism is developed for the calculation of absorption of radiation by charge-transfer molecules with electronic density delocalized between the donor and acceptor parts. The theory consistently incorporates both the vibronic coupling to quantum intramolecular vibrations and electrostatic interactions with a classical polarizable medium. The formulation operates in terms of basis-invariant parameters and can be used for calculations based on both the localized diabatic states and delocalized adiabatic wave function produced by standard quantum-chemistry algorithms. The basis-invariant reorganization energy is particularly important since it determines observable spectroscopic parameters, in contrast to the adiabatic reorganization energy based on the molecular charge distributions in the adiabatic vacuum states. Analytical formulas are derived for the charge-transfer absorption band and first two spectral moments connecting spectroscopy to properties of charge-transfer molecules. Electronic delocalization requires a new definition of the Huang-Rhys factor traditionally used to construct vibronic band-shapes. Theory's performance is illustrated by application to experimental data for self-exchange charge-transfer optical absorption and for metal-to-ligand emission transitions.

Introduction

Absorption of light by molecules occurs, in the electric dipole approximation,^{1,2} due to the interaction of the dipole moment operator $\hat{\mathbf{m}}$ of the molecule with the electric (Maxwell) field of radiation $\mathbf{E}(t)$. The interaction Hamiltonian in the semi-classical approximation (classical electric field) becomes

$$\hat{H}'(t) = -\chi_c \hat{\mathbf{m}} \cdot \mathbf{E}(t) \quad (1)$$

Here, χ_c is the cavity-field susceptibility transforming the Maxwell field within a polarizable medium³ to the local field acting on the molecule.^{4,5} The quantum-mechanical perturbation theory of absorption then proceeds by assuming that the unperturbed quantum states Ψ_1, Ψ_2 belong to the manifold diagonalizing the molecular Hamiltonian and can be used to calculate the transition probability between the eigenenergies E_1 and E_2 . The energies E_1 and E_2 are the gas phase (vacuum) energies at the equilibrium geometry of the initial state 1 and the vertical energy gap $h\nu_0 = E_2 - E_1$ is the energy of light absorption in the gas phase (Figure 1). For our discussion, we will designate the basis of states Ψ_i as the adiabatic basis at the equilibrium geometry of the initial state, with a more precise definition discussed below.

This theoretical formalism is typically applied to absorption of light by molecules in the gas phase, even though the appearance of the factor χ_c in eq 1 alerts one to complications arising in

condensed materials.⁴ The fundamental difficulty arising when transitioning from the gas phase to molecules immersed in polarizable media is that the states Ψ_i have to diagonalize the Hamiltonian of both the molecule and the medium at every instantaneous statistical configuration of the latter. This is the requirement of using the interaction in eq 1 as an external perturbation, but it significantly complicates the formulation (see below). The problem does not appear as a severe complication for transitions with $h\nu_0$ far exceeding the modulation of the molecular energy levels by the medium, as quantified by the corresponding solvation free energies. Such a separation of energy scales, allowing one to view the solute-solvent interaction as a small perturbation, ceases to apply when charge-transfer transitions are concerned and when $h\nu_0$ becomes comparable or below the solvation energies involved. The theory presented here seeks a consistent formulation for the absorption of light in the latter case.

Charge-transfer molecules are composed of two units, donor and acceptor, often separated by a bridge connecting them into a molecular donor-acceptor complex. The transferring electron is partially delocalized across the molecule before the light absorption and is partially delocalized after the transition.⁶ Electronic delocalization (or valence delocalization) across the bridge creates a substantial complication for the theory since the smallness of the ratio between solvation (reorganization^{7,8}) energies and $h\nu_0$ does not apply any-

more. Every instantaneous configuration of the polarizable medium creates a different extent of electronic delocalization, leading to broad and often featureless absorption charge-transfer bands.^{9–13}

Given this difficulty, it is the opposite limit of localized electronic states that was first tackled by the theory dealing with optical absorption by localized impurities in polar materials.^{4,14–17} The Marcus theory of outer-sphere electron transfer^{8,18} was an extension of this framework allowing the electron to move its centroid of localization in a nonradiative transition driven by thermal fluctuations to achieve the tunneling configuration.^{15,19} All these models assume the ability to define diabatic, localized wave functions $\{\Psi_a, \Psi_b\}$ describing fully localized states on the donor, Ψ_a , and acceptor, Ψ_b .

A continuous transition between the limits of full localization (Robin-Day class I molecules²⁰) to full delocalization (Robin-Day class III molecules) was described by Hush⁷ in terms of two energy parameters: the electron transfer matrix element H_{ab} and the Marcus reorganization energy λ : $H_{ab}/\lambda \rightarrow 0$ specifies complete localization, while $2H_{ab} > \lambda$ leads to full delocalization. The off-diagonal matrix element $H_{ab} = \langle \Psi_a | \hat{H}_0 | \Psi_b \rangle$ is taken with the vacuum Hamiltonian \hat{H}_0 . The experimental route to this important parameter quantifying electronic delocalization was sought in terms of the Mulliken-Hush (MH) expression^{7,10,21,22}

$$H_{ab} = m_{12}(h\nu_0/\Delta m_{ab}) \quad (2)$$

Here, $\mathbf{m}_{12} = \langle \Psi_1 | \hat{\mathbf{m}} | \Psi_2 \rangle$ is the adiabatic transition dipole and $\Delta \mathbf{m}_{ab} = \langle \Psi_b | \hat{\mathbf{m}} | \Psi_b \rangle - \langle \Psi_a | \hat{\mathbf{m}} | \Psi_a \rangle$ is the change in the diabatic dipole moment. In the MH theory, it was set to represent the distance r_{ab} between centroids of electronic density on the donor and acceptor:²³ $\Delta m_{ab} = er_{ab}$.

The distance r_{ab} is not determined by the MH theory which is, therefore, incomplete. This deficiency was amended by Cave and Newton^{24,25} as follows. Prior to their Generalized Mulliken Hush (GMH) model, there was no physically-based model for defining and determining the diabatic states and the properties depending on them (especially, the donor/acceptor separation r_{ab} and Δm_{ab}). The GMH model defined the diabatic states variationally as those maximizing the diabatic dipole difference, Δm_{ab} (i.e., by diagonal-

izing the dipole matrix). With the diabatic states (a,b) thus in hand, the non-perturbative GMH algorithm allows one to calculate Δm_{ab} through m_{12} and the change in the adiabatic dipole moment $\Delta \mathbf{m}_{12} = \langle \Psi_2 | \hat{\mathbf{m}} | \Psi_2 \rangle - \langle \Psi_1 | \hat{\mathbf{m}} | \Psi_1 \rangle$ between the charge-transfer states (also see Reimers and Hush²⁶)

$$\Delta m_{ab} = [(\Delta m_{12})^2 + 4(m_{12})^2]^{1/2} \quad (3)$$

Importantly, both dipolar parameters in this equation are accessible from independent measurements.

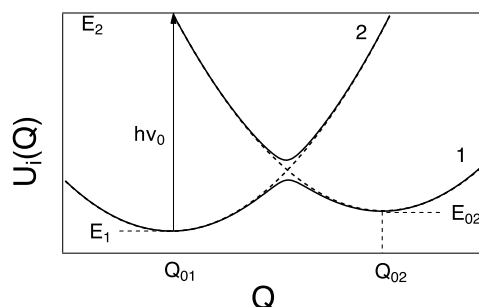


Figure 1: Schematic representation of two Born-Oppenheimer (BO) energy surfaces (solid lines) along the effective coordinate Q of intramolecular vibrations of the charge-transfer molecule. The dashed lines show shifted parabolas approximating the 3-point CA calculation (eq 14). The vertical arrow indicates the vertical energy gap $h\nu_0 = \Delta E = E_2(Q_{01}) - E_1(Q_{01})$ at the ground-state equilibrium geometry Q_{01} . The final state has the equilibrium geometry Q_{02} with the energy E_{02} such that $E_{00} = E_{02} - E_{01}$ ($E_{01} = E_1(Q_{01})$) is the 0-0 energy difference (eq 12).

As we discuss in more detail below, the product of the adiabatic vacuum transition dipole m_{12} with the adiabatic energy gap $\Delta E = h\nu_0$ can be replaced^{27–29} with the product $h\nu_{\max} m_{12}^{\max}$ of the maximum absorption frequency ν_{\max} in solution and the solution transition dipole moment m_{12}^{\max}

$$\nu_{\max} m_{12}^{\max} = \nu_0 m_{12} \quad (4)$$

One therefore arrives at a more traditional form of the MH relation⁷

$$H_{ab} = m_{12}^{\max}(h\nu_{\max}/\Delta m_{ab}) \quad (5)$$

where m_{12}^{\max} is calculated from the intensity of the optical line (see below). In addition, the differ-

ence in adiabatic dipole moments Δm_{12} in eq 3 is accessible through electroabsorption (Stark effect) spectroscopy.^{30,31}

The issues involved in connecting the theory parameters to the observable quantities,³² such as those entering the MH equation, illustrate still existing conceptual and practical problems in describing charge-transfer transitions in partially delocalized donor-bridge-acceptor systems.¹¹ Most quantum calculations are performed in the gas phase and thus produce the gas-phase adiabatic, delocalized states Ψ_i , $i = 1, 2$. However, the theory is typically formulated in terms of localized diabatic states Ψ_α , $\alpha = a, b$. Fundamentally, those localized states seem to provide more reliable representation of charge-transfer spectra.^{13,22} Therefore, connecting calculations to both the formal theory and measurements requires a separate diabaticization algorithm localizing the electronic states.²⁴ This raises the question of whether a consistent and practical theory for optical spectra in such systems can be formulated solely in terms of adiabatic electronic states.^{33–35} The goal of this study is to formulate a simple model for the band-shapes of charge-transfer transitions based on the input from adiabatic vacuum quantum states. The theory thus eliminates a separate diabaticization step required to connect adiabatic calculations to standard theories of optical and radiationless transitions formulated in terms of diabatic quantum states.

As we discuss in more detail below, the present state of the theory of charge-transfer optical bands lacks consistent account of both the intramolecular vibronic coupling and solvation by a polarizable medium. The theory presented here combines two previous developments, for charge-transfer spectra³³ and for more traditional spectroscopy of optical dyes,³⁶ to arrive at a consistent treatment of both solvent and vibronic components of charge-transfer spectra. We provide closed-form solutions for the absorption band-shape and first (band maximum) and second (band-width) spectral moments. The current formulation does not consider electronic states of the bridge and is limited to two states, which implicitly may take account of the presence of a bridge. Extensions to multiple states are possible.^{36–39}

The formalism presented here is based on the pa-

rameters of charge-transfer molecules calculated in vacuum. Inspired by the GMH framework,^{24,25} we introduce basis-invariant solvation thermodynamics involving the reaction free energy and the (free) energy of solvent reorganization. In a diabatic basis, maximizing the extent of electron localization, these basis-invariant solvation free energies become diabatic thermodynamic functions of the traditional theories operating in terms of localized states.^{14–16,40} The transformation between the adiabatic and basis-invariant thermodynamic functions is achieved in terms of the delocalization parameter

$$\Delta e = \Delta m_{12} / \Delta m_{ab} \quad (6)$$

Here, Δm_{ab} is given by eq 3 of the GMH formalism ($\Delta e = 1 - 2c_b^2$ in notation of ref 23). The delocalization parameter is thus the ratio of the adiabatic to diabatic difference dipoles: one gets $\Delta e = 1$ for transition between localized states ($m_{12} \rightarrow 0$, Robin-Day class I) and $\Delta e = 0$ for the state of complete electron delocalization ($\Delta m_{12} = 0$, Robin-Day class III). The delocalization parameter is used here to formulate a consistent theory of optical band-shapes for charge-transfer absorption in Robin-Day II and III charge-transfer complexes. The theory development is illustrated by fitting experimental charge-transfer absorption spectra.

Formalism

It is instructive to start with identifying approximations involved in the established formalisms for charge-transfer optical bands. Hush developed the first quantitative theory.⁷ His description of the crossover from charge-localized to charge-delocalized electronic configurations is based on competition between the free energy of trapping the charge by the polarizable medium (reorganization energy) and electronic delocalization between the donor and acceptor units (quantified through the energy of adiabatic splitting $2H_{ab}$). The wave functions used to produce optical extinction coefficients are gas-phase diabatic states. The formulation is, therefore, limited to the first-order perturbation theory in terms of the solute-solvent interaction: the electronic energies are permitted to change by the solvent fluctuations, but the wave functions are kept unchanged. As we show below,

this description misses an important dependence of the transition dipole on the instantaneous configuration of the solvent, which is projected onto new frequency-dependent functions (based on the experimental extinction coefficient) required to connect H_{ab} and m_{12} to absorption spectra.

The vibrational manifold of the charge-transfer molecule and its influence on optical transitions through the vibronic coupling to the normal-mode vibrations was also missing from the original Hush formulation. From the physical standpoint, this omission neglects the important effect of trapping of the electron by intramolecular reorganization (deformation of chemical bonds). The vibronic coupling was accounted for by the model proposed by Peipho, Krausz, and Schatz (PKS).⁴¹ They showed that a charge-transfer molecule can switch from charge-localized to charge-delocalized depending on the strength of the vibronic coupling or, alternatively, depending on the corresponding vibrational reorganization energy. Their theory was still based on the vacuum electronic states; that is the Hamiltonian matrix for the entire solute-solvent system was not diagonalized before considering the interaction with light given by eq 1 as the external perturbation. Similarly to the Hush theory, the PKS model is still a first-order perturbation theory in respect to the solute-solvent interaction. A consistent theory incorporating both the vibronic and solvent couplings on equal footing is required. A complete description involves the mutual modulation of solvent and vibrational nuclear modes.³⁶ Here, this complication is avoided in a mean-field fashion with the goal to arrive at closed-form expressions for absorption intensities applicable to fitting experimental spectra.

Vacuum Hamiltonian

The Born-Oppenheimer (BO) approximation solves the electronic Hamiltonian in vacuum in terms of two eigenenergies $U_i^{\text{BO}}(Q)$, $i = 1, 2$ (electronic terms) depending on the vibrational coordinate Q and serving as the potential energy surfaces for the vibrational wave functions. The standard formulation⁴² views Q as the entire manifold of molecular normal modes. Since our formulation of the vibrational Franck-Condon factor is based on a single effective vibrational mode,⁴³

Q is understood here as such an effective mode of vibrations with the effective frequency⁴⁴

$$\nu_v = \sum_j \nu_j \lambda_{vj} / \lambda_v \quad (7)$$

where the Franck-Condon active normal-mode vibrations with frequencies ν_j are combined with the corresponding vibrational reorganization energies λ_{vj} adding up to the total vibrational reorganization energy $\lambda_v = \sum_j \lambda_{vj}$ (see Supporting Information (SI) for more details and derivation).

By using the fermionic creation and annihilation operators a_i^\dagger and a_i , $i = 1, 2$ the electronic Hamiltonian becomes

$$\hat{H}_0^e = \sum_{i=1,2} U_i^{\text{BO}}(Q) a_i^\dagger a_i \quad (8)$$

The eigenenergies $U_i^{\text{BO}}(Q)$ are solutions of the BO equation with the electronic wave functions $\psi_i^{\text{BO}}(q, Q)$ depending on the electronic coordinates q and the nuclear coordinate Q . The vibronic wave functions $\Psi_{in}^{\text{BO}}(q, Q) = \psi_i^{\text{BO}}(q, Q) \chi_{in}^{\text{BO}}(Q)$ are products of $\psi_i^{\text{BO}}(q, Q)$ and the vibrational function $\chi_{in}^{\text{BO}}(Q)$.

As an illustration of the standard BO scheme, Figure 1 shows the case of near-symmetric charge transfer in vacuum. The lower surface is shown with two minima of the partially localized limit of the PKS model. This limit implies trapping of the electron on either donor or acceptor parts of the molecule by deformation (reorganization) of molecular chemical bonds. The upper surface is split from the lower surface by the donor-acceptor coupling $\simeq 2H_{ab}$. Changing the chemical identity of the donor or acceptor introduces an additional energy bias between the lower and upper surfaces, which can eliminate the second minimum on the lower surface. The potential energies are then two curves with single minima, which is the situation common to many optical transitions.

The BO approximation allows one to specify the entire double-well ground-state surface $U_1^{\text{BO}}(Q)$. However, this full description is often not needed since absorption transitions occur from states near the equilibrium geometry Q_{01} of the initial state. More importantly, the BO electronic wave functions $\psi_i^{\text{BO}}(q, Q)$ make all matrix elements based on them (such as the electric field of the charge-

transfer molecule considered below) depend on the vibrational coordinate Q . This complication makes the calculation of the absorption Franck-Condon envelope impractical. To avoid this difficulty, the crude adiabatic (CA) approximation is adopted in our analysis. This approximation is, in fact, tacitly (or explicitly^{26,45}) made by all existing models of charge-transfer optical bands. The CA approximation enters the standard formulations through the neglect of the dependence of the electronic expectation values and off-diagonal matrix elements of quantum operators on the nuclear coordinates. The CA ansatz, originally formulated by Hertzberg and Teller, separates the electronic and nuclear coordinates⁴² assuming that the electronic wave functions are taken at Q_{01}

$$\Psi_{in}(q, Q) = \psi_i(q, Q_{01})\chi_{in}(Q) \quad (9)$$

One obtains the gas-phase energies $E_i = E_i(Q_{01})$ at the equilibrium positions of the nuclei Q_{01} in the initial state (Figure 1) as solutions of the electronic eigenvalue problem

$$\hat{H}_0^e \psi_i(q, Q_{01}) = E_i \psi_i(q, Q_{01}) \quad (10)$$

The vibrational wave functions $\chi_{in}(Q)$ follow from a separate equation⁴²

$$\begin{aligned} & [T(Q) + V(Q) + E_i(Q_{01}) \\ & + \langle \psi_i | \Delta V_e | \psi_i \rangle] \chi_{in}(Q) = \epsilon_{in} \chi_{in}(Q) \end{aligned} \quad (11)$$

Here, $T(Q)$ and $V(Q)$ are the nuclear kinetic and potential energies, respectively, and $\Delta V_e(q, Q) = V_e(q, Q) - V_e(q, Q_{01})$ is the deviation of the potential energy of the electrons from the same value determined at Q_{01} ; ϵ_{in} is the total vibronic energy.

The complete solution of the nuclear dynamic problem on the lower BO surface shown by the solid line in Figure 1 has never been accomplished. One instead resorts to adopting two harmonic approximations: for the potential well near Q_{01} and for the part of the excited state surface to which the transition occurs. From the practical standpoint, a 3-point calculation can produce the ground- and excited-state parabolas. The first two calculations determine the ground-state geometry Q_{01} and two vertically displaced energies E_i . The third calculation provides the equilibrium geometry of the final state Q_{02} and the corresponding equilibrium en-

ergy E_{02} . The difference of energies between E_{02} and $E_{01} = E_1$ is the energy of the 0-0 optical transition in vacuum

$$E_{00} = E_{02} - E_{01} \quad (12)$$

Correspondingly, the vertical energy gap is

$$h\nu_0 = \Delta E = E_2 - E_1 = E_{00} + \lambda_v \quad (13)$$

This relation allows one to calculate the reorganization energy of intramolecular vibrations λ_v from known ΔE and E_{00} .

The 3-point calculation allows one to approximate the bottom part of the ground-state BO surface $U_1^{\text{BO}}(Q)$ and the portion of the upper surface $U_2^{\text{BO}}(Q)$ close to Q_{01} by two shifted parabolas

$$\begin{aligned} U_1(Q) &= E_1 + \frac{\kappa}{2} \delta Q^2, \\ U_2(Q) &= E_2 + \frac{\kappa}{2} \delta Q^2 - \kappa \Delta Q \delta Q \end{aligned} \quad (14)$$

where $\Delta Q = Q_{02} - Q_{01}$ and $\delta Q = Q - Q_{01}$ (Figure 1). They share the same force constant of harmonic vibrations κ , which also enters the vibrational reorganization energy defined in terms of ΔQ

$$\lambda_v = (\kappa/2) \Delta Q^2 \quad (15)$$

The equilibrium geometries Q_{0i} refer to adiabatic equilibrium coordinates, which can deviate from corresponding equilibrium geometries in the localized diabatic states. Therefore, if eq 15 was directly used to arrive at λ_v , it would produce the adiabatic reorganization energy λ_v^{ad} . It is also clear that this equation does not offer a practical route to calculate the vibrational reorganization energy. There is no established formalism of how to arrive at a single effective vibrational coordinate Q from displacements of either the atomic coordinates or of the corresponding normal-mode vibrations (some approaches targeting this issue have been recently suggested^{46,47}). On the other hand, since only λ_v enters the final expressions for the absorption band-shape, neither κ nor ΔQ need to be calculated. Three energies, E_i and E_{02} , from the 3-point calculation fully define the vibrational component of the band-shape for the purpose of our analysis.

One also has to realize that the reorganization en-

ergy λ_v defined through the CA energy gap ΔE carries the meaning of the vibrational reorganization energy in the localized diabatic basis.⁴¹ This is easy to realize by observing that the vertical gap ΔE in the CA basis $\psi_i(q, Q_{01})$ diagonalizes the electronic Hamiltonian and can be equally specified through the off-diagonal matrix element H_{ab} and the energy bias $\Delta I_{ab} = I_b - I_a$ of the diabatic Hamiltonian matrix

$$\Delta E = [\Delta I_{ab}^2 + 4H_{ab}^2]^{1/2} \quad (16)$$

This algebraic form is an invariant of the unitary transformation of the basis.³³ Since λ_v follows from ΔE (eq 13), which is also consistent with the standard relations used in the diabatic formulations, it refers to the localized diabatic states. Indeed, we find below that the product $\Delta e^2 \lambda_v$, corresponding to the adiabatic vibrational reorganization energy λ_v^{ad} , enters the vibronic Huang-Rhys factor as the parameter required for calculating the vibronic band-shape.

The total gas-phase Hamiltonian \hat{H}_0 in the CA approximation can be written as the sum of the harmonic vibrational Hamiltonian in the ground state $i = 1$

$$\hat{H}_v = T(Q) + (\kappa/2)\delta Q^2 \quad (17)$$

and the electronic component of the Hamiltonian defined through a_i^\dagger and a_i

$$\hat{H}_0 = \hat{H}_v + E_1 a_1^\dagger a_1 + [E_2 - \kappa\Delta Q\delta Q] a_2^\dagger a_2 \quad (18)$$

The linear in δQ term is the vibronic coupling responsible for the shift of the equilibrium position of Q upon the electronic transition.

The sequence of steps leading to the formulation of the problem in terms of two shifted vibronic parabolas has been long used in formulating theories of radiative and radiationless transitions in crystals and molecules.^{4,15,41,48} In the case of a large energy gap between the electronic states of the donor and acceptor, the second minimum of the lower potential-energy surface disappears and the two surfaces $U_i^{\text{BO}}(Q)$ can be reasonably approximated by two shifted parabolas (as is the case in our analysis of charge-transfer emission spectra discussed below). However, as is clear from Figure 1, the case of a charge transfer with $E_{00} \ll \lambda_v$ is different. Even though, the parabola $U_2(Q)$ rea-

sonably reproduces the upper BO surface, the vibrational wave functions should in fact be sought by solving the vibrational wave equation for the upper surface, which must have a significantly different force constant even if approximated by a parabola. This issue, which requires solutions going beyond the picture of shifted parabolas,⁴⁹ has not been resolved so far. We therefore employ below the traditional solution for the Franck-Condon factor of two shifted parabolas,^{4,15} with the warning that it is only an approximation requiring further improvement.

Solution Hamiltonian

The gas-phase Hamiltonian \hat{H}_0 is combined with the interaction of the electronic states with the solvent to arrive at the model of charge transfer in polarizable media. Many charge-transfer spectra are characterized by intense optical lines and large adiabatic transition dipoles. The transition dipole \mathbf{m}_{12} interacts strongly not only with the external electric field of radiation, but even to a larger extent with the much stronger internal electric field \mathbf{E}_s produced by the polarized medium. This interaction enters the theory²⁸ as the off-diagonal matrix element $\mathbf{m}_{12} \cdot \mathbf{E}_s$ of the Hamiltonian matrix. This is a non-Condon coupling between the adiabatic states,⁵⁰ which fluctuates as the medium takes different statistical configurations.

In our formalism presented here, we want to go beyond the dipolar approximation for the solute field polarizing the medium. This goal can be accommodated into the solute-bath Hamiltonian in terms of an arbitrary electric field of the donor-bridge-acceptor molecule. Applying the gas-phase CA basis $\{\Psi_1, \Psi_2\}$ described above one gets for the solute-solvent interaction

$$\hat{H}_{0s} = - \sum_{i=1,2} \mathbf{E}_i * \mathbf{P}_n a_i^\dagger a_i - \mathbf{E}_{12} * \mathbf{P}_n (a_1^\dagger a_2 + a_2^\dagger a_1) \quad (19)$$

Here, $\mathbf{E}_i = \mathbf{E}_{ii}$ is the vacuum electric field in a given CA state produced by the molecular charge distribution of the solute. The off-diagonal matrix element of the electric field operator \mathbf{E}_{12} is proportional to the adiabatic transition dipole \mathbf{m}_{12} when the solute field is approximated by that of a dipole. Finally, \mathbf{P}_n is the nuclear polarization of

the medium and asterisk denotes both the scalar product between the vector fields and integration over the bath volume.

The vector field \mathbf{P}_n here describes only the nuclear component of the medium polarization, which lags behind the fast electronic subsystem of the donor-acceptor system. The complete model requires accounting for the vector field of the electronic (fast) polarization \mathbf{P}_e as well. The full problem was considered in the past^{28,33} and here we focus only on the results of that complete derivation.

The solute-solvent Hamiltonian needs to be combined with the classical bath Hamiltonian H_s describing the free energy penalty for creating a non-equilibrium fluctuation of the medium polarization. For the latter, we adopt the standard harmonic form^{40,51}

$$H_s = \frac{1}{2\chi_n} \mathbf{P}_n * \mathbf{P}_n \quad (20)$$

in which χ_n is a scalar susceptibility describing nuclear (slow) polarization of the medium.

The polarization susceptibility χ_n represents linear response of the polar solvent to the field of the dissolved molecule (solute). It is affected by the properties of the polar solvent, the shape of the solute, and the symmetry of the charge distribution in the solute (e.g., point charge vs point dipole). In the case of the solute viewed as a spherical ion (a very unrealistic approximation for a charge-transfer molecule), $\chi_n = c_0/(4\pi)$ can be given in terms of the Pekar factor^{40,51} c_0 . This susceptibility represents the longitudinal polarization of the solvent caused by the spherically-symmetric field of the solute in the continuum limit when the dipolar correlations in the solvent are much shorter than the size of the solute. For a non-spherical solute, both longitudinal and transverse polarization components combine to produce a shape-dependent χ_n . Further, microscopic correlations between the liquid dipoles can be introduced in terms of microscopic liquid-state theories when longitudinal and transverse responses of the liquid become non-local (distant-dependent) response kernels describing the free-energy penalty of creating a medium fluctuation in terms of reciprocal-space components \mathbf{P}_k of the polarization field.^{52,53} These extensions of the theory affect the calculation of solvation energies, but otherwise are not significant to our present formulation assuming unspecified lin-

ear response functions from which solvation thermodynamics can be calculated.

The problem of activated electronic transitions is best formulated in terms of free-energy surfaces along the reaction coordinate monitoring the progress of the reaction.⁸ The reaction coordinate for a radiationless transition⁴ is the difference of two eigenenergies of the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_{0s} + H_s \quad (21)$$

depending on the classical polarization field \mathbf{P}_n ^{54,55} and quantum intramolecular vibration Q . This solution is indeed possible, but not very practical for an arbitrary off-diagonal electric field \mathbf{E}_{12} in eq 19.

The electric field \mathbf{E}_i in each adiabatic state of the molecule is easy to calculate from partial atomic charges and to incorporate into calculation algorithms for the free-energy surfaces.^{44,56} In contrast, accounting for \mathbf{E}_{12} presents significant difficulties at both the level of standard quantum algorithms and for solvation theories. In order to resolve this difficulty, one can assume³³ that \mathbf{E}_{12} is proportional to the difference of two fields in two adiabatic states, $\Delta\mathbf{E} = \mathbf{E}_2 - \mathbf{E}_1$. This field difference represents the so-called charge-transfer dipole realized by assuming that the negative electron is localized at the acceptor part of the molecule and the positive charge is placed at the donor (both charges are placed at the corresponding centroids of the electronic density).

The charge-transfer dipole is not a point dipole, but the approximation

$$\mathbf{E}_{12} = \alpha_{12}\Delta\mathbf{E} \quad (22)$$

would be exact if the solute field could be approximated by that of a point dipole. The ratio of the diagonal and off-diagonal field magnitudes can then be represented by the ratio of the corresponding dipole moments

$$\alpha_{12} = m_{12}/\Delta m_{12} \quad (23)$$

With this approximation in place, one can proceed to define the reaction coordinate

$$X = \Delta\mathbf{E} * \mathbf{P}_n - \chi_n \Delta\mathbf{E} * \mathbf{E}_m = \Delta\mathbf{E} * \mathbf{P}_n + \Delta F_n^{\text{ad}} \quad (24)$$

where $\mathbf{E}_m = (\mathbf{E}_1 + \mathbf{E}_2)/2$ is the mean electric field and $\Delta F_n^{\text{ad}} = F_{n,2} - F_{n,1}$ is the difference of nuclear solvation energies of the donor-acceptor molecule in the final and initial adiabatic states. With this definition, tracing out both the nuclear \mathbf{P}_n and electronic \mathbf{P}_e polarization fields³³ leads to the following expression for the free energy surface along the classical collective reaction coordinate X and the quantum vibrational coordinate $\delta Q = Q - Q_{01}$

$$F_{\pm}(X, Q) = X^2/(4\lambda^{\text{ad}}) \pm \frac{1}{2}\Delta E(X, Q) + \widehat{H}_v - \frac{1}{2}\kappa\Delta Q\delta Q \quad (25)$$

where

$$\Delta E(X, Q) = [(\Delta F(Q) - X)^2 + 4\alpha_{12}^2(\Delta F_s^{\text{ad}} - X)^2]^{1/2} \quad (26)$$

and

$$\Delta F(Q) = \Delta E + \Delta F_s^{\text{ad}} - \kappa\Delta Q\delta Q \quad (27)$$

Here,

$$\Delta F_s^{\text{ad}} = F_{s2}^{\text{ad}} - F_{s1}^{\text{ad}} \quad (28)$$

is the difference of full, electronic and nuclear, solvation free energies $F_{si}^{\text{ad}} = -(1/2)(\chi_n + \chi_e)\mathbf{E}_i \cdot \mathbf{E}_i$, with χ_e denoting the susceptibility of the electronic component of the medium polarization.

The adiabatic reorganization energy^{6,57} in eq 25 is given by the standard form of the solvation free energy of the charge-transfer dipole by the nuclear medium polarization

$$\lambda^{\text{ad}} = \frac{1}{2}\chi_n\Delta\mathbf{E} \cdot \Delta\mathbf{E} \quad (29)$$

However, in contrast to the Marcus reorganization energy based on localized diabatic quantum states, λ^{ad} is based on electric fields calculated from the adiabatic charge distribution. This reorganization energy can be used in calculations of optical lines involving large gas-phase energy gaps of optical dyes,³⁶ but it becomes inapplicable for self-exchange charge-transfer optical transitions between chemically equivalent donor and acceptor (λ^{ad} was given the name λ_{mod} in ref 23 and λ' in refs 6,22,58).

As we discuss in more detail below, the adiabatic reorganization energy λ^{ad} does not represent the observable properties of charge-transfer opti-

cal bands. The physically relevant parameter of charge-transfer transitions, consistent with the observed independence of the absorption maximum with respect to the extent of delocalization,^{6,22,34,58} is the basis-invariant reorganization energy, which turns into the Marcus' diabatic reorganization energy in the diabatic basis allowing maximum localization of the electron. The reorganization energy invariant to the unitary basis transformations can be identified by specifying the basis-invariant electric field $\Delta\mathbf{E}_{\alpha}^I = (\Delta E_{\alpha}^2 + 4E_{12,\alpha}^2)^{1/2}$, $\alpha = x, y, z$

$$\lambda^I = \frac{1}{2}\chi_n\Delta\mathbf{E}^I \cdot \Delta\mathbf{E}^I \quad (30)$$

By applying eq 22, the basis-invariant reorganization energy can be related to λ^{ad} through the delocalization parameter $\Delta e = [1 + 4\alpha_{12}^2]^{-1/2}$ also given by eq 6

$$\lambda^{\text{ad}} = \Delta e^2\lambda^I \quad (31)$$

Similar transformation applies to the solvation free energy³³

$$\Delta F_s^{\text{ad}} = \Delta e\Delta F_s^I \quad (32)$$

which produces the basis-invariant ΔF_s^I from the adiabatic ΔF_s^{ad} in eq 28.

Note the difference in scaling with Δe between λ^{ad} and ΔF_s^{ad} : λ^{ad} is quadratic in Δe , while ΔF_s^{ad} is linear in Δe . The difference arises from the fact that ΔF_s^{ad} is proportional to the integral $\Delta\mathbf{E}^I \cdot (\mathbf{E}_1 + \mathbf{E}_2)$ of the invariant field $\Delta\mathbf{E}^I$ with the trace, $\mathbf{E}_1 + \mathbf{E}_2$, of the 2×2 matrix of the electric field operator. Since the trace is an invariant of the unitary transformations of the basis, only a single factor Δe is needed to convert $\Delta\mathbf{E}$ to $\Delta\mathbf{E}^I$ to arrive at ΔF_s^{ad} in eq 32.

A nonlinear dependence of the energy gap $\Delta E(X, Q)$ on the quantum coordinate Q in eq 26 does not allow a closed-form solution without adopting further simplifications. Following our previous work,³⁶ we linearize $\Delta E(X, Q)$ in δQ

$$\Delta E(X, Q) = \Delta E(X) - \Delta n(X)\kappa\Delta Q\delta Q, \quad (33)$$

where $\Delta E(X) = \Delta E(X, Q_{01})$ and $\Delta n(X) = n_-(X) - n_+(X)$ is the difference of the electronic occupation numbers of the lower and upper free energy surfaces³⁶ $F_{\pm}(X) = F_{\pm}(X, Q_{01})$ (see SI).

Equation 33 carries a significant physical meaning. It implies that fluctuations of the medium

polarization change, through $\Delta n(X)$, the strength of the vibronic coupling in the molecule. As the second-order effect, not included in eq 33, the medium fluctuations alter the frequencies of quantum-mode vibrations. In order to arrive at a closed-form solution, we replace here $\Delta n(X)$ with the delocalization parameter Δe , which amounts to neglecting the fluctuations of $\Delta n(X)$ around its mean value.³³

This approximation allows us to separate $F_{\pm}(X, Q)$ into the free energy surfaces $F_{\pm}(X) = F_{\pm}(X, Q_{01})$ along the classical reaction coordinate X from the quantum vibrational Hamiltonian still accounting for the effect of delocalization on the vibronic coupling in a mean-field fashion. The result is

$$F_{\pm}(X, Q) = F_{\pm}(X) + \hat{H}_v^{\pm} \quad (34)$$

where

$$\hat{H}_v^{\pm} = \hat{H}_v \mp \frac{1}{2} h\nu_v \sqrt{S} (c^{\dagger} + c) \quad (35)$$

Here, c^{\dagger} and c are the creation and annihilation operators for the vibrational harmonic oscillator and

$$S = \Delta e^2 \lambda_v / (h\nu_v) \quad (36)$$

is the Huang-Rhys factor.¹⁵ Note the appearance of the squared delocalization parameter in front of λ_v in this equation. This scaling with the degree of delocalization is missing from the traditional theories of radiationless transitions in molecules^{4,15,17} operating with electronically localized states. This is the same scaling as the one appearing for the solvent reorganization energy in eq 31, indicating that vibronic/solvation coupling of the electron with all nuclear modes is modulated in a similar fashion by electronic delocalization.³⁶

Free-energy surfaces along X

We start our analysis with the free-energy surfaces along the reaction coordinate X defined at the ground-state vibrational geometry Q_{01} . From eqs 25 and 34, they are expressed in terms of the basis-invariant parameters (including ΔE , see eq 16) and the delocalization parameter Δe

$$F_{\pm}(X) = X^2 / (4\Delta e^2 \lambda^I) \pm \frac{1}{2} \Delta E(X) \quad (37)$$

where

$$\Delta E(X) = [\Delta E^2 + 2\Delta E(\Delta e \Delta F_s^I - X) + (\Delta F_s^I - X/\Delta e)^2]^{1/2} \quad (38)$$

We find that the vertical separation between the minima $X_{0i} \simeq \mp \Delta e \lambda^I + \Delta e \Delta F_0$ of the lower surface $F_-(X)$ is the free energy difference

$$\Delta F_0 = \Delta e \Delta E + \Delta F_s^I \quad (39)$$

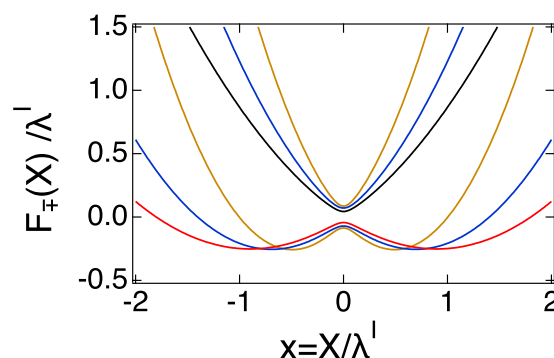


Figure 2: Upper, $F_+(X)$, and lower, $F_-(X)$, free-energy surfaces vs $x = X/\lambda^I$ (eq 37 with $C = 0$) at $\Delta e = 0.9$ (red), $\Delta e = 0.7$ (blue), and $\Delta e = 0.7$ (brown); $\Delta E/\lambda^I = 0.2$ and $\Delta F_s^I = -\Delta e \Delta E$ producing the free energy $\Delta F_0 = 0$ in eq 39.

The meaning of ΔF_0 defined here is distinct from the reaction free energy adopted in the standard theories of charge transfer.^{7,8} In those formulations, the reaction free energy ΔF_0 is the difference of free energies of the fully relaxed states, which include both the intramolecular vibrational coordinates and the nuclear polarization of the medium. Correspondingly, such an assignment requires the electronic basis set $\psi_i(q, Q_{0i})$ to be defined at equilibrium geometries of the charge-transfer molecule in the initial and final states. The electronic functions defined in this way are non-orthogonal, as was realized already by PKS.⁴¹ Non-orthogonality of the basis set creates significant difficulties for the formalism. In contrast, our choice of orthogonal CA wave functions, resolving this difficulty, is based on a single equilibrium geometry. Therefore, ΔE is a vertical transition energy and ΔF_0 in eq 39 involves relaxed states for the nuclear medium polarization, but unrelaxed (vertical) states for the intramolecular vibrational

modes. For instance, self-exchange charge transfer will have $\Delta F_s^I = 0$, but at the same time $\Delta E \simeq \lambda_v$ (Figure 1). Realizing $\Delta F_0 = 0$ thus requires a negative ΔF_s^I , which is possible only for non-symmetric charge transfer.

Figure 2 shows representative functions $F_{\pm}(X)/\lambda^I$ vs the scaled reaction coordinate $x = X/\lambda^I$. The lower surface possesses two minima at the same value of free energy when $\Delta F_s^I = -\Delta e \Delta E$ in eq 39, which is the configuration shown in Figure 2. The positions of the minima, $x_{0i} \approx \mp \Delta e$, shift closer with lowering the delocalization parameter Δe . Despite this shift, the vertical energy gap is given in term of the reorganization energy λ^I . One obtains the standard relation of the Marcus-Hush theory of charge transfer at $\Delta E/\lambda^I \ll 1$

$$\Delta E(X_{0i}) = \lambda^I \pm \Delta F_0 \quad (40)$$

where ΔF_0 is given by eq 39. Since the vertical energy gap drawn from the free-energy minimum is usually associated with an absorption transition, this equation implies that the basis-invariant reorganization energy λ^I , and not the adiabatic reorganization energy λ^{ad} , determines the transition energy. This outcome is anticipated since physical observables should not depend of the definition of the basis used in the calculations, and such an invariance is guaranteed by the definition of λ^I in eq 30.

The free energy surfaces $F_{\pm}(X)$ avoid crossing of their diabatic counterparts used in the Marcus-Hush theory of charge transfer. The minimal splitting between the upper and lower free-energy surfaces

$$E_{\text{min}} = \Delta E \sqrt{1 - \Delta e^2} \quad (41)$$

is reached at

$$X_{\text{min}} = \Delta e \Delta F_0 \quad (42)$$

The position of minimum splitting becomes $X_{\text{min}} = 0$ at $\Delta F_0 = 0$, as is shown in Figure 2.

The lower free-energy surface changes from a two-well shape to a single well at the critical value of the delocalization parameter

$$\Delta e^* = \sqrt{1 - (\lambda^I/\Delta E)^2} \quad (43)$$

signaling the transition from an electronically localized configuration to an electronically delocalized configuration.

Reaching the electronically delocalized state obviously requires

$$\Delta E > \lambda^I \quad (44)$$

This result replaces Hush's delocalization condition,⁵⁹ $2H_{ab} > \lambda$. The new delocalization criterion is the result of adding the vibronic coupling to the Hush framework operating with solvation by the medium polarization. From Figure 1, even for self-exchange charge transfer between chemically identical donor and acceptor moieties, $\Delta E \simeq \lambda_v$. Therefore, the necessary delocalization requirement in eq 44 is satisfied for self-exchange charge transfer already at $\lambda_v > \lambda^I$. If, additionally, $\Delta e < \Delta e^*$ is reached, only one minimum appears on the lower surface $F_-(X)$. This configuration of a single-minimum lower surface is realized in our analysis of charge-transfer metal-to-ligand emission discussed in more detail below, where we find $\Delta e = 0.6 < \Delta e^* = 0.98$. This limit does not, however, eliminate the possibility of two minima of the vacuum BO surface $U_1^{\text{BO}}(Q)$ along the vibrational coordinate Q (Figure 1).

Optical band-shapes

Absorption of radiation occurs due to the interaction of the molecular dipole with the field of radiation $\mathbf{E}(t) = \mathbf{E}_0 \cos \omega t$ in eq 1. Transitions at $Q = Q_{01}$ take place between adiabatic free-energy surfaces $F_{\pm}(X)$ in eq 37. In turn, $F_{\pm}(X)$ are the eigenvalues of the 2×2 Hamiltonian matrix

$$\begin{bmatrix} V_1(X) + X/2 & \alpha_{12}(\Delta e \Delta F_s^I - X) \\ \alpha_{12}(\Delta e \Delta F_s^I - X) & V_2(X) - X/2 \end{bmatrix} \quad (45)$$

with

$$V_i(X) = F_{0i}^{\text{ad}} + X^2/(4\Delta e^2 \lambda^I) + \Delta e^2 \lambda_s^I/4 \quad (46)$$

The wave functions $\{\Psi_1(X), \Psi_2(X)\}$ diagonalizing the 2×2 matrix in eq 45 are the unperturbed quantum states which can be used in the perturbation theory to calculate the transition probability with the dipole-field perturbation in eq 1. They are

connected to the gas-phase CA basis $\{\Psi_1, \Psi_2\}$ by a unitary transformation with its coefficients depending on the instantaneous configuration of the medium through the coordinate X . The transition dipole calculated with $\{\Psi_1(X), \Psi_2(X)\}$ becomes^{28,33}

$$\begin{aligned} \mathbf{m}_{12}(X) &= \langle \Psi_1(X) | \hat{\mathbf{m}} | \Psi_2(X) \rangle \\ &= \mathbf{m}_{12} \frac{h\nu_0}{\Delta E(X)} \end{aligned} \quad (47)$$

This transition dipole appears in the golden-rule expression for the transition probability leading to the following expression for the extinction coefficient of absorption^{4,9,60}

$$\frac{\epsilon(\nu)}{\nu} = \frac{4\pi^2 N_A \chi_c^2}{3000 \ln 10 \hbar c n_D} m_{12}^2 \left(\frac{\nu_0}{\nu}\right)^2 \text{FC}(\nu) \quad (48)$$

Here, the transformation from the molar concentration ($M = \text{mol/L}$) to cgs units leads to $\epsilon(\nu)$ multiplied by cm^3 and thus expressed in units cm^2/M . Further, n_D is the refractive index at the optical transition frequency; n_D^2 needs to be replaced with the real part of the medium dielectric function $\epsilon'_s(\omega)$ for lower frequencies.

The last term in eq 48 is the Franck-Condon factor given by the frequency convolution of the medium, $G_s(\nu)$, and vibrational, $G_v(\nu)$, components^{44,61}

$$\text{FC}(\nu) = \int_{-\infty}^{\infty} d\nu' (\nu/\nu')^2 G_v(\nu - \nu') G_s(\nu') \quad (49)$$

The medium Franck-Condon factor $G_s(\nu)$ is the probability of reaching resonance between the energy of the incoming photon $h\nu$ and the energy gap $\Delta E(X)$ separating $F_+(X)$ from $F_-(X)$

$$G_s(\nu) = h \langle \delta(\Delta E(X) - h\nu) \rangle_- \quad (50)$$

The average $\langle \dots \rangle_-$ is taken over the statistical configurations of the solvent when the system is in the ground state

$$\begin{aligned} \langle \dots \rangle_- &= Z_-^{-1} \int dX \dots e^{-\beta F_-(X)} \\ Z_- &= \int dX e^{-\beta F_-(X)} \end{aligned} \quad (51)$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature.

The vibrational Franck-Condon factor is given by the following relation

$$\begin{aligned} G_v(\nu) &= \int_{-\infty}^{\infty} dt e^{-i2\pi\nu t} \\ &\left\langle \hat{T} \exp \left[-i\omega_v \sqrt{S} \int_0^t d\tau (c^\dagger(\tau) + c(\tau)) \right] \right\rangle_v \end{aligned} \quad (52)$$

where \hat{T} is the time-ordering operator,^{4,62} $\omega_v = 2\pi\nu_v$, and the statistical average $\langle \dots \rangle_v$ is taken with the vibrational Hamiltonian \hat{H}_v in the ground state (eq 17).

The appearance of the frequency-dependent factor $m_{12}^2(\nu_0/\nu)^2$ in front of $\text{FC}(\nu)$ in eq 48 is the direct consequence of the variation of the transition dipole with energy gap $\Delta E(X)$ shown in eq 47. This energy gap is replaced by $h\nu'$ through the delta-function in eq 50 and one gets the factor $(\nu/\nu')^2$ under the convolution integral. Since $\nu \simeq \nu' = \langle \Delta E(X) \rangle / h$ produces the main contribution to the band-shape, we put $(\nu/\nu')^2 \approx 1$ under the integral, with a convenient result for the normalized Franck-Condon factor ($\int d\nu \text{FC}(\nu) = 1$)

$$\text{FC}(\nu) = \int_{-\infty}^{\infty} d\nu' G_v(\nu - \nu') G_s(\nu') \quad (53)$$

A solution not involving this approximation is possible, but is close to the one used here (see SI). Importantly, the $\propto \nu^{-2}$ scaling appears in front of the Franck-Condon factor without additional approximations when only the solvent effect on absorption is considered. The present form is adopted to preserve this scaling and is a very good mathematical representation of the exact result.

Physically, the appearance of the factor $m_{12}^2(\nu_0/\nu)^2$ in the extinction coefficient indicates that the transition dipole for the charge-transfer band cannot be taken in the Condon approximation neglecting its dependence on the solvent configurations. Likewise, the vibronic coupling needs to account for the effect of the solvent, which, in the mean-field fashion, results in the $\propto \Delta E^2$ scaling of the Huang-Rhys factor in eq 36. Since $\Delta E(X)$ is of the order of the solvent reorganization energy (eq 40), the transition dipoles in the solvent and in vacuum can be substantially different. On the other hand, our adoption of the CA

approximation for the basis set of electronic wave functions makes the transition dipole independent of Q . Therefore, the Condon approximation is lifted here for the solvent nuclear polarization, but is maintained for intramolecular vibrations, in line with previous studies of radiationless transitions in molecules.^{4,15,43}

Since the Franck-Condon factor $FC(\nu)$ given by eq 53 is normalized, integration over frequencies in eq 48 leads to the relation between the adiabatic vacuum transition dipole (in debye, D) and the integrated absorption band-shape

$$\nu_0 m_{12} = 9.584 \times 10^{-2} \text{ D} \left[\frac{1}{f(n_D)} \int d\nu \nu \epsilon(\nu) \right]^{1/2} \quad (54)$$

where

$$f(n_D) = \chi_c(n_D)^2 / n_D \quad (55)$$

The correction for the solvent's refractive index,⁴ $f(n_D)$, is often estimated from the electrostatic solution for the field inside a spherical cavity⁵ leading to the Onsager-type⁶³ cavity function $\chi_c(n_D) = 3n_D^2 / (2n_D^2 + 1)$. This is not the only,^{29,64} and probably not the best, approximation accounting for the local cavity field.⁶⁵ In particular, the Lorentz formula,⁵ $\chi_c(n_D) = (n_D^2 + 2)/3$, was found⁶⁶ to be a better approximation for the cavity field in liquids for the absorption of THz radiation while the Onsager model was found to be adequate⁶⁴ for radiative transitions in complexes of Eu^{3+} . The choice of the screening function does not affect the band-shape, which is our main concern here, and the Onsager cavity field was used in the calculations.

The connection between the adiabatic transition dipole and the integrated absorption band (eq 54) can be further modified by applying eq 4. A practical equation for the solution transition dipole in the MH equation (eq 5) can be derived by approximating the absorption curve $\bar{\nu}\epsilon(\bar{\nu})$ with a Gaussian function characterized by the maximum $\bar{\nu}_{\max}$ and the full width at half maximum $\Delta\bar{\nu}_{1/2}$

$$\int d\bar{\nu} \bar{\nu} \epsilon(\bar{\nu}) = \bar{\nu}_{\max} \Delta\bar{\nu}_{1/2} \epsilon_{\max} \sqrt{\pi / (4 \ln 2)} \quad (56)$$

where ϵ_{\max} is the extinction coefficient at the maximum of $\bar{\nu}\epsilon(\bar{\nu})$. Combining eqs 4, 54, and 56 one

arrives at a convenient form

$$m_{12}^{\max} = 9.888 \times 10^{-2} \text{ D} \left[\frac{\epsilon_{\max} \Delta\bar{\nu}_{1/2}}{f(n_D) \bar{\nu}_{\max}} \right]^{1/2} \quad (57)$$

where all wavenumbers are in cm^{-1} .

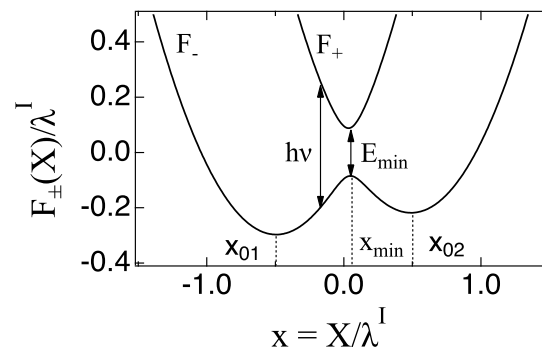


Figure 3: Upper, $F_+(X)$, and lower, $F_-(X)$, free-energy surfaces vs $x = X/\lambda^I$ at $\Delta e = 0.5$. Shown are the minimal splitting E_{\min} between the upper and lower free-energy surfaces, with the coordinate X_{\min} (eq 42); x_{0i} , $i = 1, 2$ mark the minima on the lower free-energy surface $F_-(X)$. The absorption energies $h\nu \geq E_{\min}$ are constrained to exceed E_{\min} .

We now turn to combining the solvent and vibrational components of the Franck-Condon factor in the convolution integral in eq 53. The solvent component

$$G_s(\nu) = h \sum_{k=1,2} (Z_- |\Delta E'(X_k^*)|)^{-1} e^{-\beta F_-(X_k^*)} \quad (58)$$

is calculated by solving the resonance equation $\Delta E(X_k^*) = h\nu$ in the delta-function in eq 50. Since this is a quadratic equation in terms of the variable X , two solutions generally exist (see SI)

$$X_k^* = X_{\min} \pm \Delta e \sqrt{(h\nu)^2 - E_{\min}^2} \quad (59)$$

Here, $k = 1$ and $k = 2$ correspond to “+” and “-”, respectively, and E_{\min} is the minimal splitting between $F_+(X_{\min})$ and $F_-(X_{\min})$ at the reaction coordinate X_{\min} (eqs 41 and 42). The dependence on the photon frequency in the right-hand side of eq 58 is through the roots $X_k^* = X_k^*(\nu)$. The physical meaning of this result is straightforward (Figure 3). The energy of the absorbed photon cannot be lower than the minimal splitting.^{11,34,36,67,68} There is no

solution for X at $h\nu < E_{\min}$ and the absorption intensity is identically zero below this band boundary. This constraint eliminates the red-frequency wing of the absorption spectrum, thus making the absorption band generally non-Gaussian.

Equation 58 can be further simplified when anharmonicity of the lower free-energy surface around its two minima X_{0i} can be neglected (Figure 3). The partition function Z_- in eq 51 then becomes

$$Z_- = [4\pi k_B T \lambda^I]^{1/2} (1 + g) e^{-\beta F_-(X_{01})} \quad (60)$$

where $g = \exp[-\beta \Delta F_0]$ is the ratio of populations in the two harmonic wells. The function $G_s(\nu)$ becomes a weighted sum of two Gaussian functions

$$G_s(\nu) = \frac{h}{1 + g} \left[G(\nu - \nu_{\text{abs}}^{(1)}) + g G(\nu - \nu_{\text{abs}}^{(2)}) \right] \quad (61)$$

where $h\nu_{\text{abs}}^{(i)} = \lambda^I \pm \Delta F_0$ are two absorption maxima and

$$G(\nu) = [4\pi k_B T \lambda^I]^{-1/2} e^{-\beta(h\nu)^2/(4\lambda^I)} \quad (62)$$

This limit clearly shows that both the absorption maximum of each line and its spectral inhomogeneous broadening $2k_B T \lambda^I$ are determined by the basis-invariant reorganization energy λ^I instead of its adiabatic counterpart λ^{ad} . It is therefore the former and not the latter that has to be related to the observable spectroscopic moments (see below).

The vibrational Franck-Condon factor $G_v(\nu)$ in eq 53 and 52 is well established for the problem of two shifted parabolas representing an effective skeletal vibration of the donor-acceptor molecule.^{4,15,45,48} The low-temperature solution $\beta h\nu_v \gg 2|\ln(2S)|$ is given in terms of the Huang-Rhys factor (eq 36)

$$G_v(\nu) = e^{-S} \sum_{m=0}^{\infty} \frac{S^m}{m!} \delta(\nu + \nu_v S - m\nu_v) \quad (63)$$

Plugging this result into the convolution integral in eq 53 with $G_s(\nu')$ from eq 58, one gets

$$\text{FC}(\nu) = \frac{h}{Z_-} \sum_{m=0}^{m^*} \sum_{k=1,2} \frac{e^{-S} S^m}{m!} \frac{e^{-\beta F_-(X_{km}^*)}}{|\Delta E'(X_{km}^*)|} \quad (64)$$

where

$$\Delta E'(X_{km}^*) = d\Delta E(X)/dX|_{X_{km}^*} \quad (65)$$

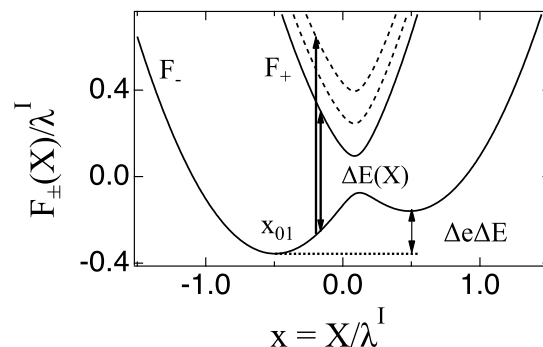


Figure 4: Upper, $F_+(X)$, and lower, $F_-(X)$, free-energy surfaces vs $x = X/\lambda^I$ at $\Delta e = 0.5$ and $\Delta F_s^I = 0$ (charge-transfer self-exchange). The radiation photon $h\nu$ excites $m = 2$ internal vibrations in the charge-transfer molecule such that the resonance condition $h\nu = h\nu_v(m - S) + \Delta E(X)$ is maintained. The free-energy difference between the minima of the free-energy surface is $\Delta F_0 = \Delta e \Delta E$.

The addition of vibrational excitations of the charge-transfer molecule to the absorption envelope leads to the modification of the resonance condition for the absorption of a photon of radiation. In addition to the condition $h\nu = \Delta E(X)$, one obtains resonances involving m vibrational quanta (Figure 4)

$$h\nu = (m - S)h\nu_v + \Delta E(X) \quad (66)$$

The solution of this equation is $X_{k,m}^*$ in eqs 64 and 65 given explicitly as

$$X_{km}^* = X_{\min} \pm \Delta e \sqrt{(h\nu + h\nu_v(S - m))^2 - E_{\min}^2} \quad (67)$$

The energy gap involving m vibrational photons still needs to be greater than the minimum splitting between the upper and lower free energy surfaces E_{\min} (Figure 3). Therefore, in contrast to the standard relations for absorption band-shapes involving an infinite number of vibrational excitations,⁴³ the sum over the vibronic transitions in eq 64 is finite. It is limited by the upper bound m^* allowing to keep the transition energy above the minimum

splitting

$$h\nu \geq h\nu_v(m^* - S) + E_{\min} \quad (68)$$

Entering the results for the Franck-Condon factor to eq 48, one obtains for the extinction coefficient of absorption

$$\bar{\nu}\epsilon(\bar{\nu}) = \frac{Af(n_D)}{1+g} \frac{\bar{\nu}_0^2 m_{12}^2}{\sqrt{\Delta e^2 \lambda^I T}} \sum_{m=0}^{m^*} \sum_{k=1,2} \frac{e^{-S} S^m e^{-\beta F_-(X_{km}^*) + \beta F_-(X_{01})}}{m! |\Delta E'(X_{km}^*)|} \quad (69)$$

where $A = 36.8357 \text{ cm}^2/\text{M}$. Further, in eq 69, $\bar{\nu} = \nu/c$ is in cm^{-1} , $\bar{\nu}\epsilon(\bar{\nu})$ on the left-hand side is in units of cm^2/M , λ^I is in cm^{-1} , m_{12} is in D and T is in K.

Figure 4 illustrates the resonance condition with the external photon involving m vibrational quanta (eq 66). Achieving this configuration requires X_{km}^* deviating from the minimum coordinate X_{0i} . The probability of this configuration is weighted with the Boltzmann factor $\exp[-\beta F_-(X_{km}^*) + \beta F_-(X_{01})]$ in eq 69. Therefore, only configurations close to the minimum X_{01} effectively contribute to the band-shape. For $S \gg 1$, $m \simeq S$ produces the highest probability of absorption,¹⁵ in accordance with the semiclassical Franck-Condon principle. The result is that the maximum frequency is $h\nu_{\max} \simeq \Delta E(X_{01})$, as we discuss in more detail below. If solvation is not involved, $X_{01} \rightarrow 0$ and $\nu_{\max} \simeq \nu_0$. Alternatively, when the vibronic coupling approaches zero, one arrives at the standard result of the Marcus-Hush theory in eq 40. We now consider a special case of self-exchange charge transfer and apply the formalism developed here to the analysis of experimental charge-transfer bands.

Charge-transfer self-exchange

The donor and acceptor parts of the charge-transfer molecule are chemically identical moieties changing their oxidation states in self-exchange charge transfer. Since this configuration is symmetric, there is no change in the solvation energy of the molecule in the charge-localized (diabatic) repre-

sentation. One therefore has to require

$$\Delta F_s^{\text{ad}} = \Delta F_s^I = 0 \quad (70)$$

From eq 39, one obtains two minima of the lower surface (Figure 4) separated by the free energy difference

$$\Delta F_0 = \Delta e \Delta E \quad (71)$$

The expression for the extinction coefficient can be somewhat simplified for self-exchange transitions, with the following result

$$\bar{\nu}\epsilon(\bar{\nu}) = \frac{Af(n_D)}{1+g} \frac{\Delta e \bar{\nu}_0^2 m_{12}^2}{\sqrt{\lambda^I T}} e^{-S} \sum_{m=0}^{m^*} \frac{S^m (\bar{\nu} + (S-m)\bar{\nu}_v)}{m!} \sum_{k=1,2} \frac{e^{-\beta F_-(X_{km}^*) + \beta F_-(X_{01})}}{|\bar{\nu}_{km} - \bar{\nu}_{\min}|} \quad (72)$$

where $hc\bar{\nu}_{km} = X_{km}^*$ (eq 67) and $hc\bar{\nu}_{\min} = X_{\min}$ (eq 42).

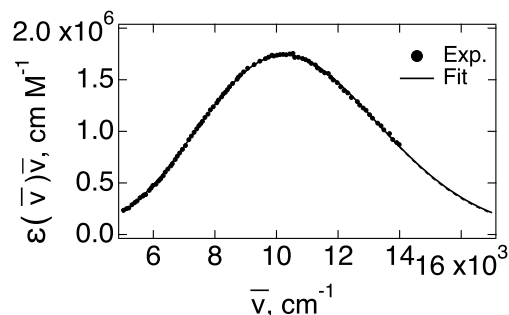


Figure 5: Experimental absorption spectrum $\bar{\nu}\epsilon(\bar{\nu})$ for a self-exchange charge-transfer transition in of 2,7-dinitronaphthalene radical anion (points,⁶⁹ exp). Experimental results are fitted to eq 72 (fit). Two fits were carried out: unconstrained fit (parameters $hc\bar{\nu}_0$, Δe , S , solid line, first row in Table 1) and a fit constrained with the condition $\Delta E = \lambda_v$ (dashed line, second row in Table 1). The dashed and solid lines are nearly indistinguishable on the scale of the plot.

Figure 5 shows the application of eq 72 to the optical spectrum of 2,7-dinitronaphthalene radical anion reported in ref 69. Integrating the experimental absorption band (points in Figure 5) approximated by a sum of two Gaussian yields the transition dipole $m_{12}^{\max} = 1.05 \text{ D}$ at $\bar{\nu}_{\max} = 10183 \text{ cm}^{-1}$ (eqs 4 and 54). Two fits of the experimental

band were attempted. We first performed an unconstrained fit by varying four parameters: $\Delta E = hc\bar{\nu}_0$, Δe , S , and λ^I while keeping the effective vibrational frequency at⁷⁰ $\bar{\nu}_v = 1300 \text{ cm}^{-1}$. The vibrational reorganization energy λ_v was calculated from Δe , S , and ν_v by using eq 36. These results are shown by the first row in Table 1. The second fit applied the constraint $\Delta E = \lambda_v$ expected for self-exchange transitions (Figure 1). These results are given by the second row in Table 1, and the best fit is achieved at $\Delta e = 0.99$. Both procedures produce nearly equal quality of the fit. This outcome illustrates uncertainties of unconstrained fits when applied to the analysis of charge-transfer spectra.

For the parameters listed in Table 1, the weight of the second absorption line g is negligible and only $k = 1$ in eq 72 effectively contributes to the absorption profile. Nevertheless, the skewness built in the band-shape through the combination of the lower band boundary $h\nu_{\min} = E_{\min}$ and vibrational excitations of the upper free-energy surface is sufficient to obtain a perfect fit of the experimental band-shape. The asymmetry of the experimental absorption band had puzzled the researchers in the past, and an empirical quartic term (in addition to the Marcus parabola) was introduced⁶⁹ to the charge-transfer free-energy surfaces to account for this effect. The present model avoids these artificial constructs and provides perfect account of the experimental band-shape within an exactly solvable two-state model allowing electronic delocalization between the donor and acceptor parts of the molecule.

Table 1: Parameters of fitting the optical spectrum⁶⁹ shown in Figure 5 (energy parameters are in cm^{-1}).^a

ΔE	Δe	λ^I	λ_v	S
4393	0.92	6643	5526	3.6
4829	0.99	5917	4823	3.7

^aexperimental data are reported in acetonitrile as a solvent at 293 K.

Metal-to-ligand transition

Fitting of the absorption spectrum for charge-transfer self-exchange (Figure 5 and Table 1)

yields $\Delta e > 0.92$. This nearly complete charge transfer does not allow a critical test of the theory. We therefore turn to metal-to-ligand spectra for which emission lines have been long used to access parameters of charge-transfer transitions.^{13,71} Previously reported analysis of the solvent-dependent absorption of $[\text{Ru}(\text{bpy})_3]^{2+}$ applied the Onsager model of dipole solvation⁶³ allowing one to extract the difference of dipole moments in the excited and ground states. Since the absorption band is specified by basis-invariant solvation parameters, the dipole moment difference obtained from these data corresponds to the GMH difference dipole in eq 3: $\Delta m_{ab} = 14 \text{ D}$.^{13,72} On the other hand, electroabsorption measurements on $[\text{Ru}(\text{bpy})_3]^{2+}$ produced⁷³ $\Delta m_{12} \simeq 7.3 \text{ D}$. Given uncertainties with assigning the cavity field susceptibility χ_c affecting interpretation of electroabsorption data, one obtains from eq 6 the delocalization parameter $\Delta e \simeq 0.54 - 0.6$.⁷³ Here we show that this extent of charge delocalization is consistent with fitting of the emission band-shape^{13,70} to the present model.

Charge-transfer emission measures the number of photons $I_{\text{em}}(\nu)$ emitted per unit frequency such that the radiative rate is^{1,27,28,34} $k_{\text{rad}} = \int d\nu I_{\text{em}}(\nu)$. The formalism developed here for absorption of radiation is equally applicable to radiation emission. Because of the dependence of the two-state transition dipole on the photon frequency (eq 47), the emission spectrum is proportional to the product of the emission frequency and the Franck-Condon factor³⁴

$$I_{\text{em}}(\bar{\nu}) \propto \bar{\nu} \text{FC}_{\text{em}}(\bar{\nu}) \quad (73)$$

where $\text{FC}_{\text{em}}(\bar{\nu})$ is given by the convolution of the solvent and vibrational envelopes, eq 53. Calculation of the emission spectrum requires a statistical average taken over the equilibrium distribution specified by the upper surface F_+ in eq 58. Additionally, the resonance condition $\nu + \nu_v S - m\nu_v$ for the vibrational component in eq 63 changes to $\nu - \nu_v S + m\nu_v$. Furthermore, the vacuum energy gap at the equilibrium geometry of the excited state becomes $\Delta E = E_{00} - \lambda_v$. The vacuum energy gap for the ligand-to-metal photon emission in $[\text{Ru}(\text{bpy})_3]^{2+}$ far exceeds λ_v , which implies that there is only one minimum on the lower BO surface in vacuum and the picture of two shifted parabolas applies to this problem.

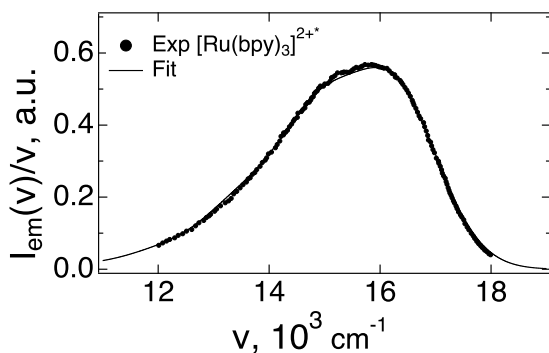


Figure 6: Emission band $I_{\text{em}}(\bar{\nu})/\bar{\nu}$ of photoexcited $[\text{Ru}(\text{bpy})_3]^{2+*}$ (points, arbitrary units) fitted to eq 73 with the following fitting parameters: $\Delta e = 0.60$, $\nu_0 = 13774$, $\lambda^I = 2983$, $\lambda_v = 3432$, $\Delta F_s^I = 4157$, and $\bar{\nu}_v = 1300$ (all energy parameters are in cm^{-1}). Experimental data are collected in acetonitrile at 298 K.

Integrated emission can be used to calculate the transition dipole moment³⁴ (in debye, D)

$$\bar{\nu}_0 m_{12} = \frac{3.09 \times 10^8}{\chi_e \sqrt{n_D}} \left[\int (d\bar{\nu}/\bar{\nu}) I_{\text{em}}(\bar{\nu}) \right]^{1/2} \quad (74)$$

This calculation is not attempted here since only emission profiles are available to us. Figure 6 shows the experimental emission band-shape of photoexcited $[\text{Ru}(\text{bpy})_3]^{2+*}$ (points, arbitrary units) plotted according to eq 73 as $I_{\text{em}}(\bar{\nu})/\bar{\nu}$. The solid line shows the fit of the experimental curve to the theoretical $\text{FC}(\bar{\nu})$, which indeed results in $\Delta e \simeq 0.60$ in accord with the above estimate.

The dependence of the transition dipole on the instantaneous energy gap (eq 47) alters the frequency prefactor in eq 73 and the dependence of the radiative transition rate on the average emission frequency. The standard theories for radiation emission in vacuum predict¹

$$k_{\text{rad}} \propto m_{12}^2 \langle \nu^3 \rangle \quad (75)$$

arising from $I_{\text{em}}(\nu) \propto \nu^3$. In this equation, the average over the emission band-shape is defined as

$$\langle \nu^n \rangle = \int_{-\infty}^{\infty} d\nu \nu^n \text{FC}(\nu) \quad (76)$$

In contrast, accounting for the dependence of the transition dipole on the photon frequency (eq 47)

leads to the frequency scaling in eq 73 and a different result for the radiative rate (in s^{-1})

$$k_{\text{rad}} = 3.14 \times 10^{-7} n_D \chi_c^2 m_{12}^2 \bar{\nu}_0^2 \langle \bar{\nu} \rangle \quad (77)$$

where m_{12} is in debye and the wavenumbers are in cm^{-1} . Therefore, a linear scaling of the radiative rate with the transition frequency is predicted

$$k_{\text{rad}} \propto m_{12}^2 \langle \bar{\nu} \rangle \quad (78)$$

Such a linear scaling between the radiative rate and the emission frequency was indeed reported for colloidal CdSe and CdTe quantum dots.⁷⁴

Discussion

A complete analysis of the optical band-shape is often circumvented by using the band maximum and width to extract the reorganization parameters and the extent of electron delocalization. The extension of the Hush model⁷⁵ for intervalence optical band-shapes to the present model involving both the vibronic and solvent effects on the band-shape makes many of these simplified recipes inapplicable.

From the convolution relation for the Franck-Condon factor, one obtains for the first spectral moment in eq 76 (see SI)

$$h \langle \nu \rangle = \langle \Delta E(X) \rangle_- \quad (79)$$

Since the optical band-shape is asymmetric, the first spectral moment somewhat deviates from the absorption maximum. Neglecting this deviation, and replacing the average energy gap with that at the minimum X_{01} of the lower free-energy surface $F_-(X)$, $\langle \Delta E(X) \rangle \simeq \Delta E(X_{01})$, one obtains for self-exchange charge transfer ($\Delta F_s^I = 0$)

$$h\nu_{\text{max}} = [\Delta E^2 + 2\Delta e \Delta E \lambda^I + (\lambda^I)^2]^{1/2} \quad (80)$$

where we assumed $X_{01} \simeq -\Delta e \lambda^I$. This is a good approximation at $\Delta E/\lambda^I < 0.5$ for the numerical solution of the equation for X_{01}

$$\Delta E(X_{01}) = \lambda^I (1 - X_{\text{min}}/X_{01}) \quad (81)$$

Equation 80 converts at $\Delta e = 1$ to the commonly anticipated¹² additivity of the vibrational

and solvent reorganization energies to the absorption maximum

$$h\nu_{\max} = \lambda^I + \lambda_v + E_{00} \quad (82)$$

where eq 13 was used to express ΔE in terms of the 0-0 transition energy E_{00} and the reorganization energy λ_v . At an arbitrary value of the delocalization parameter Δe , there is no arithmetic additivity between the solvent and vibrational components in the absorption maximum and either the approximate analytical result in eq 80 or a direct numerical solution of eqs 79 and 81 should be used instead.

Repeating the above procedure for the second spectral cumulant, one obtains (see SI)

$$h^2\langle\delta\nu^2\rangle = \Delta e^2 h\nu_v \lambda_v + \langle\delta\Delta E(X)^2\rangle_- \quad (83)$$

where $\delta\nu = \nu - \langle\nu\rangle$ and $\delta\Delta E(X) = \Delta E(X) - \langle\Delta E(X)\rangle_-$. This equation employs the effective vibrational frequency ν_v as defined by eq 7. This definition of the effective frequency ensures that the second spectral cumulant carries the same value in the effective-frequency representation, as given by eq 83, and in the more complete description through all normal-mode frequencies ν_j with their corresponding reorganization energies λ_{vj} (see SI). Since the first spectral moment is fixed by the average vertical gap (eq 79) and does not involve any properties of the vibronic envelope, the effective-frequency formalism establishes the invariance of the first two spectral moments between the reduced and full descriptions. Given that two first spectral moments often suffice to reproduce the band-shapes, this invariance might be the reason for the well-documented success of the effective-frequency description of optical spectra.^{36,43,47,76}

A definition of the average vibrational frequency alternative to eq 7 has been offered in the literature^{47,70,71,76-78}

$$\nu_v = \frac{\sum_j \nu_j S_j}{\sum_j S_j} \quad (84)$$

Here, the normal-mode frequencies are weighted with partial Huang-Rhys factors $S_j = \lambda_{vj}/(h\nu_j)$ (alternatively, the mean frequency $\nu_v = N^{-1} \sum_j \nu_j$ was used in ref 45 even though based

on the short-time expansion as in our definition, see SI). The approach specified by eq 84 to calculating ν_v is only an empirical approximation which, importantly, does not preserve the invariance of the second spectral cumulant between the effective-frequency representation and a full calculation involving the entire spectrum of normal modes.

The variance of the energy gap $\Delta E(X)$ in the last term of eq 83 can be estimated as $2k_B T \lambda^I$. One therefore gets for the the full width at half maximum

$$h^2\Delta\nu_{1/2}^2 = 8 \ln(2) [h\nu_v \Delta e^2 \lambda_v + 2k_B T \lambda^I] \quad (85)$$

The relation derived by Hush⁷⁵ (self-exchange) is often used instead⁷⁰

$$h^2\Delta\nu_{1/2}^2 = 16 \ln(2) k_B T h\nu_{\max} \quad (86)$$

The Hush relation can only be recovered if intramolecular reorganization energy is put equal to zero. In a general case, there is no direct relation between the band maximum in eq 80 and the band width in eq 85. In fact, eq 85 predicts an upward deviation of the bandwidth from the Hush equation, as is often reported experimentally.^{57,71,79,80}

The vibronic component of the bandwidth, originating from quantum vibrations, is temperature independent (first term in eq 85). Equation 85, therefore, provides a simple recipe to extract λ^I and $h\nu_v \lambda_v$ from, correspondingly, the slope and intercept of $h^2\Delta\nu_{1/2}^2$ vs T . This analysis is complicated by the fact that the solvent reorganization energy also changes with temperature.^{44,81} Nevertheless, published data on the temperature dependence of the absorption width for self-exchange charge-transfer complexes^{80,82} are clearly inconsistent with eq 86. Instead, $h^2\Delta\nu_{1/2}^2$ vs T shows a large positive intercept roughly consistent with eq 85 (two self-exchange radical cation systems in acetonitrile in Figure 7; also see Figure 7 in ref 80 for metal-to-ligand transitions).

Equation 85 predicts that the band-width should decrease when the charge is more delocalized, or less trapped by the medium polarization, thus leading to a smaller Δe . This result is a direct consequence of the modulation of the vibronic coupling by electronic delocalization³⁶ and the result-

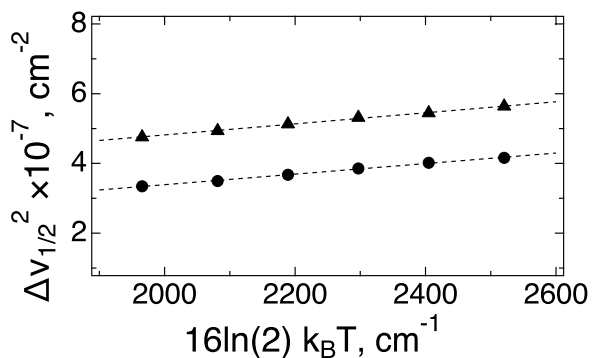


Figure 7: $\Delta\bar{\nu}_{1/2}^2$ vs $16 \ln(2)k_B T$ for self-exchange charge-transfer radical cations in acetonitrile studied in ref.⁸² Results for two complexes are shown: with 2,5-xylylene-1,4-diyl bridge (circles) and durene-1,4-diyl bridge (triangles). The slopes of the plots are 15122 (circles) and 15858 (triangles) cm^{-1} . The values of $\Delta e^2 \lambda_v$ are estimated from the intercept by applying eq 85. They are 826 (circles) and 3709 (triangles) cm^{-1} based on $\bar{\nu}_v = 800 \text{ cm}^{-1}$.

ing new definition of the Huang-Rhys factor (eq 36). The delocalization parameter Δe (eq 6) quantifies the extent of electron trapping by the polarizable medium in competition with the resonance energy $2H_{ab}$ tending to delocalize the electron. We can re-write eq 6 in terms of parameters commonly reported for charge-transfer molecules

$$\Delta e = \frac{\Delta m_{12}}{m_{12}^{\max}} \frac{H_{ab}}{h\nu_{\max}} \quad (87)$$

Note that charge localization by intramolecular vibrations does not affect Δe . Whether the charge is trapped on one side of the molecule (two minima of the lower BO surface, Figure 1) or is delocalized across the charge-transfer molecule (one minimum on the lower BO surface) in vacuum is fully determined by the solution of the vacuum vibronic coupling model.

The connection between the adiabatic and basis-invariant (analog of the diabatic Marcus-Hush) reorganization energies deserves special comment. Equation 31 connecting the adiabatic reorganization energy to the diabatic (Marcus-Hush) reorganization energy (λ^I here) was previously derived^{22,58} in terms of the squared delocalization parameter given by the following expression:⁵⁸

$1 - 4H_{ab}^2/(\lambda^I)^2$. This recipe makes the delocalization parameter a solvent-dependent property, with no clear relation between λ^{ad} and λ^I . In contrast, our delocalization parameter Δe connecting two reorganization energies in eq 31 is defined in terms of the vacuum diabatic and adiabatic difference dipole moments (eq 6), with no solvation effects involved. Summarizing the results of the bandshape analysis (eqs 31 and 87), a relation between λ^{ad} and λ^I can be cast in terms of observable spectroscopic parameters

$$\lambda^I = \left(\frac{m_{12}^{\max} h\nu_{\max}}{\Delta m_{12} H_{ab}} \right)^2 \lambda^{\text{ad}} \quad (88)$$

We finally note that equilibrium statistics of both the intramolecular vibrations and medium polarization was used in the present analysis. A connection between radiative and radiationless charge-transfer transitions has not been considered here. For many sufficiently slow reactions, the parameters extracted from optical bands can be applied to the calculation of reaction rates.^{10,27,75} However, for fast reactions, the time-scale of transition can potentially cut into the spectrum of solvent fluctuations, resulting in the dynamic freezing of at least a subset of solvent modes.^{11,83} Dynamic freezing of nuclear motions leads to narrowed optical bands when nuclear fluctuations cannot contribute to broadening on the time-scale of electronic transitions. This type of systems, characterized as Robin-Day II-III,¹¹ requires explicit account of characteristic time-scales in the analysis of radiationless transitions.

Conclusions

Closed-form expressions for the absorption of radiation by charge-transfer molecules are derived here. While carrying many of the elements of classical theories of optical absorption by localized electronic states,^{4,15,48} our approach presents important extensions to electronically delocalized states coupled vibronically to intramolecular normal-mode vibrations and interacting electrostatically with a polarizable medium. Intramolecular vibrations are represented by an effective quantum mode and the medium polarization is

represented by linear susceptibilities which can be used both in continuum and microscopic solvation theories. Solvent-induced electronic delocalization affects the vibronic envelope in terms of the delocalization parameter entering the new definition of the Huang-Rhys factor in eq 36.

From the standpoint of the electronic structure of the charge-transfer molecule, the theory is formulated in terms of basis-invariant parameters, which allow the use of standard quantum-chemistry algorithms in vacuum for the calculation of spectral band-shapes of charge-transfer molecules in polarizable media. The basis-invariant reorganization energy is particularly important since it determines observable spectroscopic parameters, in contrast to the adiabatic reorganization energy based on direct vacuum calculation of the molecular charge distribution. The two reorganization energies are related through the delocalization parameter Δe (eq 6). It can be viewed as an independent fitting parameter for the analysis of band-shapes, but is also accessible by experiment. The absorption band-shape turns out to be asymmetric, in agreement with observations.

Supporting Information Available

Derivation of free-energy surfaces of electron transfer, optical band-shapes for absorption, Franck-Condon factors, and the effective frequency for intramolecular vibrations.

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