A Failure of Continuum Theory: Temperature Dependence of the Solvent Reorganization Energy of Electron Transfer in Highly Polar Solvents

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The temperature dependence of the solvent reorganization energy for intramolecular electron transfer (ET) in acetonitrile is measured experimentally and calculated theoretically. The Stokes shifts for the charge transfer, optical transitions of (tetrahydro-4H-thiopyran-4-ylidene)propanedinitrile indicate that the solvent reorganization energy for ET decreases with temperature, whereas dielectric continuum theories of solvent reorganization predict an increase with temperature. A molecular alternative to the continuum description is proposed that models the solvent as a fluid of polarizable, dipolar hard spheres. Good agreement between the molecular theory and experiment is achieved for both the ET reorganization energy and equilibrium energy gap. The negative temperature slope of the solvent reorganization energy is understood in terms of its dissection into components arising from different solute−solvent interaction potentials and contributions from different solvent modes activating ET. In the first approach, we consider reorganization energy components from permanent and induced dipoles. In the second dissection, the orientational and density solvent fluctuations are considered. The analyses show that the molecular nature of the solvent, embodied in density fluctuations and associated translational motions of the solvent permanent dipoles, is the principal source of the negative temperature dependence of the solvent reorganization energy. This component is absent in the continuum picture. Its absence is the reason the continuum model fails to correctly predict the sign of the reorganization energy temperature dependence in polar solvents.

1. Introduction

Electron transfer (ET) reactions are activated by thermal fluctuations of solvent and solute nuclear modes interacting with the electronic density at the donor and acceptor sites. This interaction is realized, for the most part, through Coulomb forces between the charges localized on the solvent molecules and the electron attending transfer. The parameter quantifying the energetic scale of solvent fluctuations is the solvent reorganization energy λ_s. The enormous influence of solvent activation on ET kinetics and charge transfer optical spectra in condensed phases has motivated numerous theoretical calculations and experimental measurements of λ_s.[1]

The Marcus model of solvent reorganization[2] represents the microscopic field of the solvent acting on the transferred electron by a cavity field of a dielectric continuum. The model is very useful[1] and provides many important insights into solvent effects on the activation barrier for ET and other types of reaction[3] in polar liquids. It is exceptional to have a description of solvent reorganization in terms of only two, well-tabulated, bulk solvent parameters: the refractive index and the static dielectric constant. On the other hand, this concept suggests that ET reactions (and, more generally, reactions producing changes in solute multipole state), interact only with the macroscopic electric field in a polar medium. Clearly, the reaction proceeds on a molecular length scale and is coupled to specific molecular motions of the solvent as well as to the macroscopic electric field. This raises a fundamental question: Which activation parameters probe

predominantly the macroscopic electric field and which are affected by specific molecular structural features and motions? The answer to this question will help define the limitations of the continuum picture and provide indications of where to look for evidence of molecular solvent effects on chemical reactivity. The present paper is a development in this direction. Dielectric continuum models do not predict the proper temperature dependence of the solvent reorganization energy in highly polar solvents: the continuum model predicts an *increase* in the reorganization energy with temperature in contrast to the spectroscopically observed *decrease* with temperature. A molecular alternative to the dielectric continuum model is therefore proposed that more adequately reproduces the experimental results. The model gives spectroscopic parameters in terms of temperature dependent dielectric and density properties of the solvent.

Solvation is a major source of the temperature dependence of the electron transfer activation barrier which is determined by the equilibrium free energy gap ΔF_0 and the reorganization energy λ. The latter is the sum of the intramolecular vibrational reorganization energy λ_v, and λ_s: $\lambda = \lambda_v + \lambda_s$. Therefore, to understand or predict the temperature variation of the ET rate constant, one needs the temperature dependence of both the equilibrium energy gap ΔF_0 and the solvent reorganization energy λ_s. This information is difficult to extract by fitting rate constants[4] or optical bandshapes,[5] as the effects of ΔF_0 and λ_s on these observables are highly correlated. An experimental

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solution to this difficulty is to measure the temperature dependence of both the charge transfer absorption $\hbar\omega_{abs}(T)$ and emission $\hbar\omega_{em}(T)$ energies. Their difference is equal to twice the total reorganization energy[6,7]

$$\lambda = \lambda_s + \lambda_v = (\hbar/2)[\omega_{abs}(T) - \omega_{em}(T)] \qquad (1)$$

and their mean is the energy gap

$$\Delta F_0 = (\hbar/2)[\omega_{abs}(T) + \omega_{em}(T)] \qquad (2)$$

In the absence of thermochromic data, a reliable theoretical treatment is needed to predict the temperature dependence of ΔF_0 and λ_s. As we show below, continuum models are not very dependable for this purpose and an alternative molecular theory is sought. Theories incorporating various levels of sophistication may be chosen. Detailed interaction potentials are presently available for many molecular fluids.[8] These can be used to calculate spectroscopic and ET parameters by using integral equation theories[9] or computer simulations.[10,11] An alternative approach is to employ relatively simple solvent models that reproduce the important solvation physics and that can be formulated in terms of easy-to-use and intuitively transparent algorithms. In this paper, we follow the latter approach and use the simplest molecular alternative to the dielectric continuum: a solvent of polarizable, dipolar hard spheres. This model includes two physically important features of molecular liquids that are absent in the continuum picture: the finite size of the solvent molecules and thermal translational modes resulting in density fluctuations.[12] Accordingly, we address the basic question of this investigation: Is the explicit inclusion of translational motions of the solvent sufficient to correct the failure of continuum dielectric theories in describing the temperature dependence of ΔF_0 and λ_s?

Although the molecular model of dipolar fluids is appealing, there are limitations to its applicability. The attractive branch of the intermolecular potential is oversimplified. Two important components not included are the dispersion attraction[13] and the interaction with solvent molecular quadrupoles. Both factors can substantially modify the solvation thermodynamics,[9b,12c,d,14,15] especially for solvation in weakly polar solvents.[9b,16] Neglect of dispersion turns out not to be a major problem as these interactions do not result in a noticeable reorganization energy,[12d] and their contribution to the equilibrium energy gap is nearly independent of temperature.[12c] The absence of quadrupolar interactions in the model limits the choice of solvents for comparison. The spectroscopic data must be derived from a solvent with the smallest possible component of quadrupole solvation. Acetonitrile appears to satisfy this requirement. Among molecular liquids, acetonitrile has the smallest ratio of the reduced quadrupole and permanent dipole moments $(Q^*/m^*)^2 = 0.024$. Here, $(m^*)^2 = \beta m^2/\sigma^3$, $(Q^*)^2 = \beta Q^2/\sigma^5$, m is the solvent permanent dipole, σ is the solvent hard sphere (HS) diameter,[17] Q is the projection of the axial quadrupole moment on the direction of the solvent dipole,[18] and $\beta = 1/k_BT$. The ratio of dipole−quadrupole and dipole−dipole solvation energies can be estimated as[14,19]

$$2r_{0s}^{-4/3}(Q^{*2}/m^{*2}) \qquad (3)$$

where $r_{0s} = R_0/\sigma + 1/2$ is the reduced distance of the closest approach of the solute and solvent hard cores and R_0 is the solute HS radius. For the chromophore used in the present study, $r_{0s} \cong 1.6$ and quadrupole solvation is not expected to exceed 2% of the solvation energy arising from the solvent permanent dipoles.

The remainder of the paper is organized as follows. In the next section the procedure employed to calculate the ET solvent reorganization energy and equilibrium energy gap is described. In section III, we compare the continuum and molecular theories of solvent reorganization to experiment. Section IV draws conclusions.

2. Calculation Procedure

2.1. Reorganization Energy and Free Energy Gap. The semiclassical approximation, assuming classical character of the system nuclear modes, produces the following relation for the frequency profile of the ground state $(i = 1)$ optical absorption band ("abs") and for the charge transfer state $(i = 2)$ emission band ("em")[20]

$$I_{abs,em}(\omega) = \int_{-\infty}^{\infty} \exp(-i\hbar\omega\xi)I_i(\xi)d\xi/2\pi \qquad (4)$$

Here the generating function

$$I_i(\xi) = Q_i^{-1}\mathrm{Tr}(\exp[i\Delta E\xi - \beta E_i]) \qquad (5)$$

with

$$Q_i = \mathrm{Tr}(\exp[-\beta E_i]) \qquad (6)$$

indicates that electronic transitions take place predominantly when the energy of the incident light $\hbar\omega$ is close to the instantaneous free energy gap $\Delta E = E_2 - E_1$ at the equilibrium configuration of the nuclear subsystem. "Tr" in eq 5 refers to the integral over the positions and orientations of the solvent molecules. The instantaneous free energies E_i, depending on the nuclear configuration, are obtained by adiabatic elimination of the electronic degrees of freedom of the solvent and the solute that are fast compared to the characteristic frequency of the electronic transition of the solute.[21,22]

A neutral optical chromophore with a permanent dipole moment interacts with a polar solvent via several potentials. A significant portion of the interaction energy is produced by coupling of the solute permanent dipole moment to the permanent dipoles of the solvent. This dipole−dipole interaction potential $U_{p,i}$ is proportional to the solute dipole moment $\mathbf{m}_{0i}$ and can be written as

$$U_{p,i} = \mathbf{m}_{0i} \cdot \sum_j \mathbf{u}_p(0j) \qquad (7)$$

where "0" stands for the solute and the sum runs over all the solvent molecules. Adiabatic elimination of rapidly fluctuating induced dipoles of the solvent and the solute generates the induction $U_{ind,i}$ and dispersion $U_{disp,i}$ solute−solvent potentials.[21e] The former is proportional to m_{0i}^2, and the latter scales as the solute polarizability α_{0i}

$$U_{ind,i} = m_{0i}^2 \sum_j u_{ind}(0j) \qquad (8)$$

$$U_{disp,i} = \alpha_{0i} \sum_j u_{disp}(0j) \qquad (9)$$

In eqs 7−9 the functions $\mathbf{u}_p$, u_{ind}, and u_{disp} denote the parts of the corresponding solute−solvent interaction potentials remaining after extracting the factors $\mathbf{m}_{0i}$, m_{0i}^2, and α_{0i}, respectively. These functions are independent of the dipole moment and polarizability of the solute. This observation enables us to write the generating functions $I_i(\xi)$ in terms of solvation chemical

potentials arising from effective, complex-valued interaction potentials. For example, for the solute−solvent dipole−dipole interaction potential, the combination of $i\xi\Delta E$ and $-\beta E_i$ terms in eq 5 produces the effective interaction potential

$$(\mathbf{m}_{0i} - i\xi\Delta\mathbf{m}/\beta)\cdot\sum_{j} \mathbf{u}_{\mathrm{p}} \tag{10}$$

The instantaneous free energies include the vacuum electronic energy levels I_i, the above potentials, and the solvent−solvent interaction energy U_{ss}

$$E_i = U_{\mathrm{ss}} + I_i + U_{\mathrm{p},i} + U_{\mathrm{ind},i} + U_{\mathrm{disp},i} \tag{11}$$

The generating function assumes the form[15,23]

$$I_i(\xi) = Q_i^{-1} \exp [i\Delta I\xi - \beta\mu_{\mathrm{p}}(\tilde{\mathbf{m}}_{0i}) - \beta\mu_{\mathrm{ind}}(\tilde{\mathbf{m}}_{0i}^2) - \beta\mu_{\mathrm{disp}}(\tilde{\alpha}_{0i})] \tag{12}$$

where

$$Q_i = \exp [-\beta\mu_{\mathrm{p}}(\mathbf{m}_{0i}) - \beta\mu_{\mathrm{ind}}(m_{0i}^2) - \beta\mu_{\mathrm{disp}}(\alpha_{0i})] \tag{13}$$

In eq 12, $\Delta I = I_2 - I_1$, μ_{p}, μ_{ind}, and μ_{disp} are the chemical potentials of solvation by permanent dipoles, inductions, and dispersion forces, respectively. They are taken as functions of complex-valued dipole moments $\tilde{\mathbf{m}}_{0i} = \mathbf{m}_{0i} - i\xi\Delta\mathbf{m}/\beta$, $\tilde{m}_{0i}^2 = m_{0i}^2 - i\xi(m_{02}^2 - m_{01}^2)/\beta$, and the complex-valued polarizability $\tilde{\alpha}_{0i} = \alpha_{0i} - i\xi\Delta\alpha/\beta$, where $\Delta\mathbf{m} = \mathbf{m}_{02} - \mathbf{m}_{01}$ and $\Delta\alpha = \alpha_{02} - \alpha_{01}$. In the present paper, we will assume that the solute polarizability does not change in the course of an electronic transition $\alpha_{01} = \alpha_{02} = \alpha_0$ and will focus only on the effect of the change in the solute dipole on the reorganization and equilibrium solvation energetics.[24]

A Gaussian spectral line is produced by keeping the terms of the first order, $\propto\xi$, and second order, $\propto\xi^2$, in the exponent of the generating function in eq 12. We, therefore, need to include only the expansion terms of the first and the second order in the corresponding solute−solvent potentials when considering the chemical potentials μ_{p} and μ_{ind}

$$\mu_{\mathrm{x}} = \mu_{\mathrm{x}}^{(1)} + \mu_{\mathrm{x}}^{(2)} \tag{14}$$

with x = p or ind. Due to the angular anisotropy of the dipole−dipole potential, the first-order term disappears in the expansion of μ_{p} in $U_{\mathrm{p},i}$ and we get the standard linear response result[12c,25]

$$\mu_{\mathrm{p}} = -(af - a_{\mathrm{ind}}f_{\mathrm{ind}}) (\mathbf{m}_{0i} - i\xi\Delta\mathbf{m}/\beta)^2 \tag{15}$$

Here, the response of the permanent solvent dipoles is expressed as the difference between the total linear response function a of the induced and permanent dipoles and the linear response function of the induced dipoles a_{ind}. The response functions a and a_{ind} are the linear response scaling terms connecting the solvation chemical potentials μ and μ_{ind} to the squared solute dipole, $\mu = afm_0^2$ and $\mu_{\mathrm{ind}} = a_{\mathrm{ind}}f_{\mathrm{ind}}m_0^2$. The chemical potential measures the solvation power of both the induced and permanent dipoles; μ_{ind} arises from the induced dipoles only.

In eq 15, the quantity

$$f = [1 - 2\alpha_0 a]^{-1} \tag{16}$$

is responsible for the renormalization of the solute dipole by the total reaction field of the solvent, including the effect of the induced and permanent dipoles. The solute permanent dipole is renormalized by the solvent field through production of an

induced solute dipole. The solute's permanent and fluctuating induced dipoles sum and the action of the solute on the solvent can be represented by an effective permanent dipole that is larger than the vacuum value m_0 by the factor f: $m_0' = fm_0$. Correspondingly, the renormalization factor

$$f_{\mathrm{ind}} = [1 - 2\alpha_0 a_{\mathrm{ind}}]^{-1} \tag{17}$$

reflects the action of the inertialess solvent field arising from the induced dipoles *only*.

For the induction potential both the first and the second-order terms of the expansion of μ_{ind} in $U_{\mathrm{ind,I}}$ are nonzero

$$\mu_{\mathrm{ind}} = -a_{\mathrm{ind}} f_{\mathrm{ind}}(m_{0i}^2 - i\xi(m_{02}^2 - m_{01}^2)/\beta) - b_{\mathrm{ind}}f_{\mathrm{ind}}^2 (m_{0i}^2 - i\xi(m_{02}^2 - m_{01}^2)/\beta)^2 \tag{18}$$

where b_{ind} is the second-order induction response coefficient. b_{ind} is the scaling factor relating the chemical potential of induction solvation to the fourth power of the solute dipole.

When the expansions of μ_{p} (eq 15) and μ_{ind} (eq 18) are used in the generating function $I_i(\xi)$ (eq 12), the terms linear in ξ produce the position of the spectral line

$$\hbar\omega_{\mathrm{abs}} = \Delta F + \lambda_{\mathrm{s}}, \quad \hbar\omega_{\mathrm{em}} = \Delta F - \lambda_{\mathrm{s}} \tag{19}$$

Equation 19 generates eqs 1 and 2 for the case of zero intramolecular reorganization. Here, the free energy gap

$$\Delta F = \Delta I + \Delta F_{\mathrm{s}} \tag{20}$$

is composed of the vacuum gap ΔI and the difference of the solvation free energies for the excited and ground states

$$\Delta F_{\mathrm{s}} = -af(m_{02}^2 - m_{01}^2) - b_{\mathrm{ind}}f_{\mathrm{ind}}^2 (m_{02}^4 - m_{01}^4) \tag{21}$$

Since the first-order response of the solvent induced dipoles is included in the response function a, ΔF_{s} contains both the first- and second-order induction response coefficients a_{ind} and b_{ind}.

Terms quadratic in ξ in the expansions of μ_{p} and μ_{ind} given by eqs 15 and 18 produce the solvent reorganization energy

$$\lambda_{\mathrm{s}} = \lambda_{\mathrm{p}} + \lambda_{\mathrm{ind}} \tag{22}$$

The first term λ_{p} is the reorganization energy associated with rotations and translations of the solvent permanent dipoles. It has been derived previously in the literature as[12c,25]

$$\lambda_{\mathrm{p}} = (\Delta m)^2[af - a_{\mathrm{ind}} f_{\mathrm{ind}}] \tag{23}$$

The second term in eq 22 is the solvent reorganization energy of the induced dipoles

$$\lambda_{\mathrm{ind}} = b_{\mathrm{ind}} f_{\mathrm{ind}}^2 (m_{02}^2 - m_{01}^2)^2 \tag{24}$$

Both components of the solvent reorganization energy λ_{p} and λ_{ind} are produced by two types of solvent thermal fluctuations: translations and rotations of the solvent dipoles. Thermal motions of the permanent dipoles directly affect the solute-solvent potential producing the component λ_{p}. Since isotropically polarizable solvent molecules instantaneously adjust their induced dipoles to the external field, no contribution to the reorganization energy comes from the first order response term ($\propto a_{\mathrm{ind}}$) that generates the induction potential. The second-order response ($\propto b_{\mathrm{ind}}$), however, yields the component λ_{ind} that is produced by (i) translations modifying the solute−solvent

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induction potential and (ii) fluctuations of the local field of the induced solvent dipoles reorienting the solvent induced dipole.[15a]

In the dielectric continuum model, the solvation response does not include translations of the induced solvent dipoles and only reorientations of the permanent solvent dipoles contribute to λ_s.[26] In this model, the coefficients a and a_{ind} factor into geometric R_c and polarity Ψ^c and Ψ^c_{ind} components, i.e.,

$$a = R_c^{-3}\Psi^c, \quad a_{ind} = R_c^{-3}\Psi^c_{ind} \tag{25}$$

where R_c is the radius of a cavity cut off from the dielectric continuum by the solute and the response functions Ψ^c and Ψ^c_{ind} are given solely in terms of the static ϵ_s and high-frequency ϵ_∞ solvent dielectric constants

$$\Psi^c = \frac{\epsilon_s - 1}{2\epsilon_s + 1}, \quad \Psi^c_{ind} = \frac{\epsilon_\infty - 1}{2\epsilon_\infty + 1} \tag{26}$$

The molecular theory used here as an alternative to the continuum description is a system composed of a dipolar, polarizable HS solute in a liquid of dipolar, polarizable hard spheres. To calculate the reorganization energy λ_p, one needs the linear response functions a and α_{ind}. Among the several means available for this calculation, we employ the Padé-truncation of the perturbation expansion for the solvation chemical potential.[27] The method is analytically simple, straightforward to use and produces results that agree well with computer simulations.[27c] For a spherical solute, the Padé linear response coefficient a can be split, analogously to eq 25, into effective radius and polarity terms

$$a = R_{eff}^{-3}(\rho^*,r_{0s}) \, \Psi^P(y,\rho^*,r_{0s}) \tag{27}$$

In contrast to continuum theories, where the cavity radius R_c is treated as solvent independent, the effective solute radius, R_{eff} in eq 27, is a function of the reduced solvent density $\rho^* = \rho\sigma^3$ and of the reduced distance of the solvent closest approach $r_{0s} = R_0/\sigma + 0.5$, where ρ is the solvent number density. R_{eff} is equal to $R_{0s} = R_0 + \sigma/2$ at $\rho^* \to 0$ and is less than that for nonzero solvent densities. The effective radius is expressed in terms of the pair distribution function $g_{0s}^{(0)}(r)$ of solvent HS cores against the solute HS by the relation

$$R_{eff}^{-3} = 3 \int_0^\infty \frac{dr}{r^4} g_{0s}^{(0)}(r) \tag{28}$$

The polarity response function Ψ^P in eq 27 can be formulated as a Padé form

$$\Psi^P(y,\rho^*,r_{0s}) = \frac{y}{1 + \kappa(\rho^*,r_{0s})y} \tag{29}$$

in the dipolar density of a polarizable fluid

$$y = (4\pi/9)\beta m'^2 \rho + (4\pi/3)\rho\alpha \tag{30}$$

Here m' is the condensed phase dipole moment of the solvent molecules and α is their polarizability. The parameter $\kappa(\rho^*,r_{0s})$ in eq 29 determines the saturation of the one-particle solvent response due to three-particle solute−solvent−solvent correlations.[27]

To calculate the response of the inertialess, electronic component in the expression of the reorganization energy (eq 23), the permanent solvent dipole is set equal to zero in the total solvent response in eqs 27 and 30. This gives the response

coefficient a_{ind} in the form

$$a_{ind} = R_{eff}^{-3}(\rho^*,r_{0s}) \, \Psi^P(y_e,\rho^*,r_{0s}) \tag{31}$$

with

$$y_e = (4\pi/3)\rho\alpha \tag{32}$$

Since the polarity parameter y_e is small, the screening effect of the solvent induced dipoles is weak and the denominator in the Padé form Ψ^P (eq 29) can be neglected. With good accuracy we thus get

$$a_{ind} = \frac{1}{R_{eff}(\rho^*,r_{0s})^3} \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \tag{33}$$

where the Clausius−Mosotti relation

$$y_e = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \tag{34}$$

was used instead of eq 32. Equation 33 indicates that solvation by induced solvent dipoles behaves as if the induced solvent dipoles form a continuous medium. The effective "cavity" radius R_{eff} of the solute in this continuum is produced by the local packing of the solvent molecules around the solute.

The polar component of the solvent response does not behave in a continuum-like fashion because the many-body screening of the direct solute-solvent interaction becomes increasingly important with increasing y. This effect dominates at high solvent polarities resulting in saturation of the solvent response. In that limit ($y \to \infty$ in eq 29), the polar solvent response is determined solely by the solvent density and the relative sizes of the solute and the solvent, i.e., $\kappa(\rho^*,r_{0s})^{-1}$. The solvent reorganization of permanent dipoles involves both a and a_{ind} response coefficients. The expression for λ_p follows from eqs 23, 27, and 31 and reads

$$\lambda_p = \frac{(\Delta m)^2}{R_{eff}^3}[f(y)\Psi^P(y) - f(y_e)\Psi^P(y_e)] \tag{35}$$

where

$$f(y) = \left[1 - \frac{2\alpha_0}{R_{eff}^3}\Psi^P(y)\right]^{-1} \tag{36}$$

Here, for brevity, the dependence of R_{eff} and Ψ^P on the solvent density and the solute reduced size have been omitted. Similarly, the component of the equilibrium energy gap $\Delta F_s^{(1)}$ due to first-order induction and dipolar solvation is given by

$$\Delta F_s^{(1)} = -\frac{(m_{02}^2 - m_{01}^2)}{R_{eff}^3} f(y)\Psi^P(y) \tag{37}$$

The second-order induction coefficient b_{ind} was calculated in refs 12c and 15 and is given by the relation

$$b_{ind} = \frac{\beta}{200\pi\rho} \frac{(\epsilon_\infty - 1)^2}{(\epsilon_\infty + 2)^2}[9 + 8(\epsilon_\infty - 1)^2] I_{0s}^{(4)} \tag{38}$$

where the perturbation integral $I_{0s}^{(4)}$ (tabulated in ref 27a) is

$$I_{0s}^{(4)} = 9 \int_0^\infty \frac{dr}{r^{10}} g_{0s}^{(0)}(r) \qquad (39)$$

The induction reorganization energy is calculated by combining eqs 24 and 38. The solvation component of the free energy gap (eq 21) is given by the sum of the first-order term in eq 37 and the second-order induction contribution

$$\Delta F_s^{(2)} = -(m_{02}^4 - m_{01}^4) f(y_e)^2 b_{ind} \qquad (40)$$

with b_{ind} from eq 38.

2.2. Solvent Parameters. The total dipolar density y (eq 30) and the polarizability contribution y_e (eq 32) are required to calculate the response coefficients a_p and a_{ind}. The latter is easily obtained, either directly from eq 32 or from the Clausius−Mosotti relation (eq 34). Both methods give very similar results. The total dipolar strength parameter y is not as straightforward to calculate because y depends on the condensed phase value of the dipole moment m' rather than the vacuum value m. The renormalization of the solvent dipole moment by the field of the surrounding solvent molecules is of the same physical origin as the renormalization of the solute dipole moment discussed above. In the former case, the mutual, many-body coupling of the solvent induced dipoles necessitates solution of a self-consistent equation to calculate m' from m. The Wertheim theory[28] provides a means of calculating m' and Gray, Gubbins, and co-workers have published a convenient numerical recipe for this renormalization.[29] Nonetheless, this procedure is complicated and it is desirable to have a simpler method for determination of the parameter y in practical applications. This can be achieved through the Kirkwood relation

$$\frac{(\epsilon_s - 1)(2\epsilon_s + 1)}{9\epsilon_s} = g_K y \qquad (41)$$

with the Kirkwood factor g_K estimated from the Kirkwood−Fröhlich equation

$$g_K = \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{y_0 \epsilon_s (\epsilon_\infty + 2)^2} \qquad (42)$$

where

$$y_0 = (4\pi/9)\beta m^2 \rho \qquad (43)$$

is the dipolar density of the solvent permanent dipoles.

Table 1 lists values of y calculated using the Wertheim theory and eqs 41−43 for several polar solvents. Because we are interested in the temperature dependence of spectral parameters, the temperature derivatives $T(dy/dT)_P$ predicted by eqs 41−43 and the Wertheim theory are also listed in Table 1. The temperature derivative $T(dy/dT)_P$ is taken at constant pressure and thus includes thermal expansion of the liquid solvent. In order to calculate y, the density variation in y_0 (eq 43) was approximated as varying linearly with temperature,

$$\rho(T) = \rho_0(T_0) [1 - \alpha_p(T - T_0)] \qquad (44)$$

where α_p is the isobaric thermal expansion coefficient and T_0 = 298 K. Analogously, the temperature dependent dielectric constants ϵ_s and ϵ_∞ were calculated as

$$\epsilon_{s,\infty}(T) = \epsilon_{s,\infty}(T_0) + (d\epsilon_{s,\infty}/dT)(T - T_0) \qquad (45)$$

using experimental temperature derivatives. The same temper-

TABLE 1: Dipolar Strength Parameters (Equation 30) and Their Temperature Derivatives at T_0 = 298 K for Different Solvents

solvent	Wertheim theory		Kirkwood−Fröhlich equation	
	y	$T_0(dy/dT)$	y	$T_0(dy/dT)$
tetrahydrofuran	1.32	−1.97	1.48	−2.21
acetone	3.99	−6.99	3.51	−5.66
dimethylsulfoxide	6.37	−9.18	6.88	−10.07
dimethylformamide	7.69	−11.49	7.28	−10.66
acetonitrile	10.73	−16.77	9.55	−15.95
propionitrile	11.32	−16.37	10.84	−15.60

CHART 1
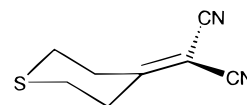
ature dependence of the density was used with the Wertheim approach for determination of $T(dy/dT)_P$. As is seen in Table 1, eqs 41−43 predict both the values of the polarity parameter y and its temperature derivative, relatively accurately. This algorithm of calculating y greatly simplifies calculation of the reorganization energy and its temperature dependence. Thus, the overall procedure for analysis of the experimental data employs eqs 35 and 36, with the parameter y derived from eqs 41−43 and the electronic polarity parameter y_e from either eq 32 or eq 34, to calculate λ_p and eq 24 to calculate λ_{ind}.

The temperature dependent liquid density entering R_{eff} and Ψ^P functions may be taken from experiment or estimated according to eq 44. There is one complicating factor. R_{eff} and $\kappa(\rho^*,r_{0s})$ in eq 29 depend on the reduced density $\rho^* = \rho\sigma^3$, and the temperature dependence of the HS diameter $\sigma(T)$ should be taken into account in calculating $\rho^*(T)$. The linearized form for $\rho^*(T)$ is

$$\rho^*(T) = \rho^*(T_0) [1 - (T - T_0)(\alpha_p - (3/\sigma(T_0))(d\sigma/dT))] \quad (46)$$

Unfortunately, $d\sigma/dT$ magnitudes are unknown for most molecular liquids. We can estimate the error resulting from use of constant σ. For instance, $T(d\sigma/dT) = -0.25$ Å was reported for dichlormethane.[30] With $\sigma = 4.62$ Å the term $-(3/\sigma)(d\sigma/dT) = 0.54 \times 10^{-3}$ K^{-1} is approximately 40% of the expansibility coefficient of dichlormethane $\alpha_p = 1.35 \times 10^{-3}$ K^{-1}. Neglecting the temperature dependence of the solvent HS diameter produces too small of a temperature variation of $\rho^*(T)$. Fortunately, R_{eff} and $\kappa(\rho^*,r_{0s})$ depend weakly on the reduced density. Thus, inclusion of $\sigma(T)$ does not significantly alter the final results for the solvation thermodynamic parameters. The main source of the temperature effect comes from the parameters of dipolar strength y and y_e (see below) which do not depend on $\sigma(T)$.

3. Results

The solute employed in this study is (tetrahydro-4H-thiopy-ran-4-ylidene)propanedinitrile (Chart 1).[31] This is one of a small number of σ-conjugated donor−acceptor molecules that exhibits both charge-transfer absorption and charge-transfer emission spectra. Figure 1 presents the experimental absorption and emission spectra of this chromophore in acetonitrile. In Figure 2 we show experimental (points) and calculated (lines) temperature dependences of the solvation reorganization energy λ_s and the solvation component $-\Delta F_s$ (eq 20) of the equilibrium energy gap. The solvent parameters used in the calculations are listed in Table 2. The solution equilibrium energy gap was
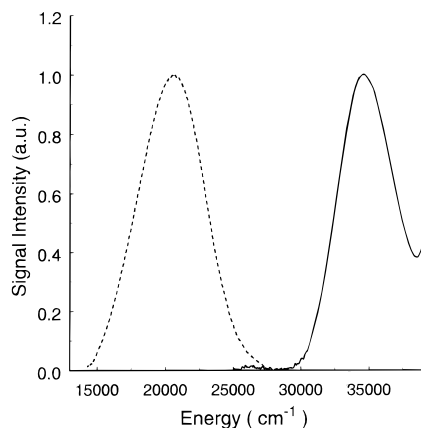
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Figure 1. Experimental charge transfer absorption (solid) and emission (dashed) bands of (tetrahydro-4H-thiopyran-4-ylidene)propanedinitrile in acetonitrile at 300 K.
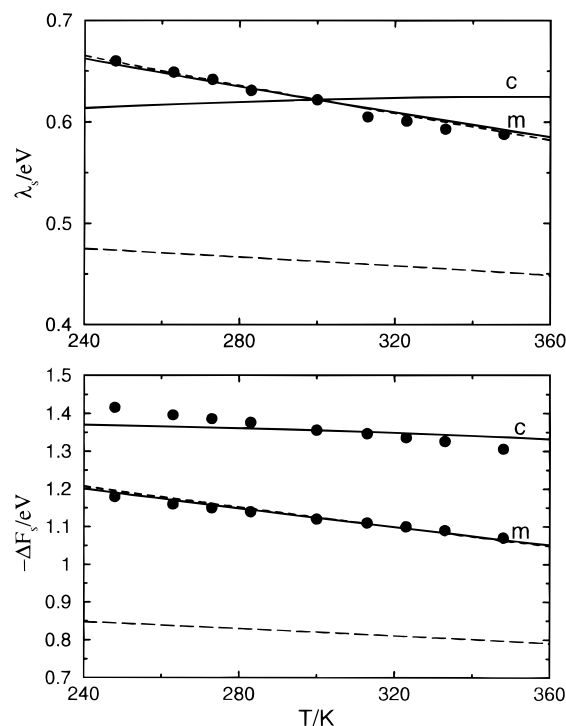

Figure 2. λ_s (upper panel) and $-\Delta F_s$ (lower panel) calculated in the continuum (c) and molecular (m) models in acetonitrile as a solvent. The overlapping solid and dash-dotted lines refer to the slopes predicted by the Wertheim theory and the Kirkwood–Fröhlich equation, respectively. The points indicate experimental results. The long dashed lines indicate the molecular calculation without the density component in both λ_s and $-\Delta F_s$. The two sets of experimental points in the lower panel correspond to the molecular and continuum estimates of the vacuum gap ΔI (Table 3).

TABLE 2: Solvent Parameters Used in the Calculations

solvent	ϵ_∞	ϵ_s	$\partial\epsilon_\infty/\partial T \times 10^3$ K	$\partial\epsilon_s/\partial T$ K^{-1}	$\alpha_p \times 10^3$ K	m, D	σ, Å	α, Å^3
acetonitrile	1.80	35.9	−1.21	−0.155	1.38	3.9	4.14	4.48

determined as the mean of the reduced[32] absorption and emission band maxima according to eq 2. The evaluation of ΔI is described below. The spectral Stokes shift is determined by both the solvation reorganization energy and the vibrational reorganization energy λ_v. The temperature dependence of λ_s in Figure 2 was derived using $\lambda_v = 0.45$ eV.[33] This value was determined from AM1 calculations as the energy increase attending distortion of the ground state from its equilibrium geometry to

TABLE 3: Comparison of the Molecular and Continuum Treatments of the Reorganization Energy and Equilibrium Energy Gap Temperature Dependence

	$R_{0,c}^a$, Å	ΔI, eV	$T_0(\partial\lambda_s/\partial T)_P^b$, eV			$T_0(\partial\Delta F_s/\partial T)_P$, eV		
			or.^{c}	dens^c	total^c	or.^{c}	dens^c	total^c
continuum	4.52	4.64	0.03	0	0.03	0.10	0	0.10
molecular	4.50	4.39	−0.06	−0.13	−0.19	0.14	0.23	0.37
experiment					−0.23			0.32

^{a} Hard sphere radius in the molecular theory and the cavity radius in the continuum model at $T_0 = 300$ K; the effective radius R_{eff} in the molecular model is 5.68 Å at 300 K. ^{b} The subscript "P" stands for isobaric conditions. ^{c} Orientational (λ_s^{or}, "or.") and density (λ_s^{dens}, "dens") components of the reorganization energy and free energy gap ("total").

the equilibrium geometry of the radical cation (0.33 eV) plus the energy required to distort the ground state to the equilibrium geometry of the radical anion (0.12 eV).[34]

The vacuum values of the ground m_{01} and charge-transfer state m_{02} dipole moments are 3.9 and 19.0 D, respectively. The angle between $\mathbf{m}_{01}$ and $\mathbf{m}_{02}$ is 16°. To complete the calculations of the reorganization energy, one also needs to determine (i) the solute polarizability α_0 and (ii) an effective radius R_0 of the sphere representing the nonspherical chromophore. The former quantity, calculated using the Miller[35] algorithm of additive atomic hybrid polarizabilities, amounts to $\alpha_0 = 17$ Å^3. With the other quantities in hand, the experimental $T = 300$ K value of $\lambda_s = 0.62$ eV was used to determine the effective radius of the molecule $R_0 = 4.50$ Å. With this effective radius, $\Delta F_s = -1.11$ eV at 300 K. From this value and the experimental, 300 K free energy gap $\Delta F_0 = 3.28$ eV, the vacuum energy gap was determined to be $\Delta I = 4.39$ eV. The temperature dependences of both λ_s and ΔF_s were calculated with no additional adjustable parameters. Similar values of the cavity radius $R_c = 4.52$ Å and the vacuum energy gap, $\Delta I = 4.64$ eV were obtained from an analogous analysis using continuum Onsager functions (eq 26) in eqs 21 and 23. A similar estimate of the cavity radius $R_c = 4.50$ Å is provided by the Gaussian 98 package (MP2 level with full geometry optimization in the 6-31G* basis set). Table 3 gives a summary of the fitting parameters derived from the 300 K data using the molecular and continuum models.

At first glance, the similarity of the effective solute radius R_0 and the cavity radius R_c is surprising. Continuum models tend to overestimate the solvation response of a dipolar solvent, and as a result, continuum models normally produce cavity radii that are larger than molecular radii.[27c] In the approach used in this investigation, the similarity of the extracted radii arises from the vastly different sensitivities to the solvent polarizability found in the continuum and molecular models of the solvent reorganization energy.[11a,d] In continuum models, the solvent reorganization energy is diminished by values of ϵ_∞ greater than 1. Moderate solvent polarizability significantly reduces the predicted solvent reorganization energy (see eqs 32 and 34) which, in this analysis, leads to a smaller cavity radius. By contrast, molecular models predict that the solvent reorganization energy is nearly independent of α. Figure 3 shows the dependence of λ_s and $-\Delta F_s$ on α predicted by the molecular model employed in this analysis (solid lines) and by the continuum model (dashed lines).[36] The weak variation of λ_s with increasing α in the molecular description results from nearly complete cancelation of two effects of the polarizability: a reduction of λ_p due to increased a_{ind} (eq 23) and a corresponding increase of λ_p due to the increase of the total response a arising from a higher effective solvent dipole m' (eqs 27 and 30). Figure 3 shows that the continuum model prediction of the reorganiza-
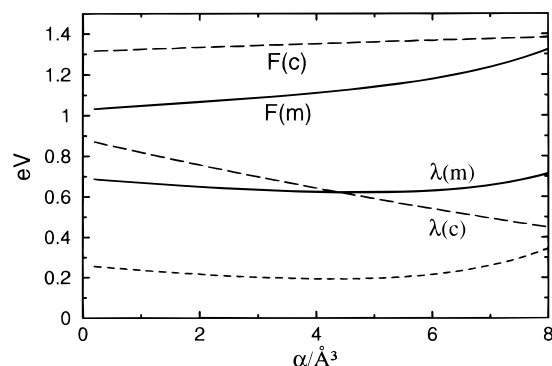
Figure 3. λ_s (λ) and $-\Delta F_s$ (F) vs the solvent polarizability α. The solid lines refer to calculations with the molecular model (m), dashed lines represent the continuum model (c) with the high-frequency dielectric constant obtained from α according to eqs 32 and 34. The static dielectric constant is obtained by varying ϵ_∞ in the Kirkwood–Fröhlich equation (eq 42) with the constant value of $y_0 g_K$ characteristic of acetonitrile. The short-dashed line indicates $-T(\partial \lambda_s/\partial T)_P$ obtained with the molecular λ_s. All solvent and solute properties except α are the same as those listed in Tables 2 and 3.

tion energy is much higher than the molecular model prediction in a nonpolarizable, dipolar solvent ($\alpha = 0$). For highly polarizable, dipolar solvents, the continuum reorganization energy may be comparable to or less than the molecular prediction.

The temperature variations of λ_s and $-\Delta F_s$ were calculated using the Wertheim theory (solid lines in Figure 2) and the Kirkwood–Fröhlich equation (eqs 41 and 42, dash-dotted lines in Figure 2) using the corresponding, best fit values of the effective solute radius (the fitted radius in the Kirkwood-Fröhlich formulation $R_0 = 4.49$ Å is very close to $R_0 = 4.50$ Å in the Wertheim theory). The difference in the calculated values of λ_s and $-\Delta F_s$ using the two methods does not exceed 1%, and the two calculated curves are almost indistinguishable on the scale of Figure 2. The effect of changing the solvent HS diameter σ with temperature was also explored by performing the same calculations using $T(\text{d}\sigma/\text{d}T) = -0.2$ Å. These results are very close to those obtained using $T(\text{d}\sigma/\text{d}T) = 0$ and are indistinguishable on the scale of Figure 2. Consequently, the temperature variation of σ can be ignored in calculations of λ_s and ΔF_s and their temperature dependences. The *variations* of both λ_s and $-\Delta F_s$ with T are reasonably reproduced by the present theory (Figure 2 and Table 3). In contrast, the continuum model (eqs 21, 23, and 26) predicts an incorrect temperature dependence for λ_s: the continuum calculation predicts that λ_s *increases* with temperature whereas the experimental λ_s *decreases* (Figure 2 and Table 3).

The fluid of dipolar polarizable spheres (and generally any fluid of rigid molecules) has two modes of thermal nuclear motion: rotations and center of mass translations. Accordingly, the response function $R_{\text{eff}}^{-3}\Psi^P$ includes two components: the liquid response due to changes of molecular orientations and the response due to changes of molecular positions in the solute vicinity (referred to as a structural response). Calculation of the reorganization energy using perturbation expansions for the attractive and repulsive solute−solvent potentials (represented by Mayer functions) produces, respectively, orientational and density reorganization terms[12a,b]

$$\lambda_s = \lambda_s^{\text{or}} + \lambda_s^{\text{dens}} \tag{47}$$

The first component λ_s^{or} arises from the orientational (longitudinal and transverse) structure factors of polarization fluctuat-

ions,[12c] whereas the second component λ_s^{dens} originates from the density structure factor of solvent density fluctuations.

In constructing the Padé form used here, a more traditional approach was employed: the expansion was performed over only the solute−solvent multipolar potential. The density structure factor enters the response function through the solute−solvent, spherically symmetric pair correlation function $h_{0s}(r) = g_{0s}(r) - 1$ within the perturbation integrals (eqs 28 and 39). The orientational solvent response can be extracted by assuming $h_{0s}(r) = 0$ which is equivalent to taking $\rho^* = 0$ in $R_{\text{eff}}(\rho^*, r_{0s})$ (eq 28) and in $\kappa(\rho^*, r_{0s})$ (eq 29).[37] The long-dashed lines in Figure 2 represent λ_s and $-\Delta F_s$ that arise from *only* the orientational solvent response (orientational reorganization[12a,b]). This calculation demonstrates that the response component due to the solute−solvent structure (density reorganization[12a,b]) makes a significant $\simeq 25\%$ contribution to both λ_s and $-\Delta F_s$. A qualitatively similar result arises from studies of solvent dynamics of multipole solvation (see ref 38 and references therein). As in this study of equilibrium solvent reorganization, rotational solvent modes are the main factor determining the energetics of the dynamic solvent response (the contribution of rotational modes compared to translational modes declines with increasing solvent and solute mulitpoles[38b]).

4. Discussion

In the Introduction, the basic question of the present study was formulated: can a simple model of a dipolar liquid with molecular translations remedy the deficiency of the continuum picture in describing the effect of temperature on ET activation parameters? Our results suggest a positive answer to this question. Despite this model's simplicity, the calculated and experimentally derived temperature dependence of the reorganization energy and the equilibrium energy gap are in good agreement. It is important to stress that the values of R_0 and ΔI are fixed by the experimental values of λ_s and ΔF_0 at 300 K. The *temperature dependence* of λ_s and ΔF_0 are predicted by the molecular model with *no additional adjustable parameters*.

The present work emphasizes the importance of thermochromic experiments in testing theoretical models of solvent reorganization in chemical reactions. All available theories of ET solvent reorganization contain some flexibility in the choice of parameters (e.g., solute hard sphere or cavity radius) that allows close agreement between theory and experiment under a specific set of conditions. Once a parameter set is chosen, however, a self-consistent theory should predict *variations* of the observable quantities with external parameters (temperature, pressure, solvent, etc.). In this regard, thermochromic data are of tremendous importance in elucidating fundamental limitations of a theory, e.g., of the continuum picture in favor of molecular descriptions. Experimentally, the reorganization energy in highly polar solvents *decreases* with temperature, whereas continuum models predict an *increase*. It should be noted that an increase of λ_s with T is predicted by continuum theories for both the intermolecular (Born-like (ion) solvation model) and intramolecular (Onsager (dipole) reaction-field model) configurations of the ET system.

The thermochromic results presented in this paper seem to be the first direct experimental evidence of the temperature dependence of the reorganization energy for intramolecular ET in a highly polar solvent. Negative temperature dependence of λ_s was previously reported for several chromophores based on analyses of absorption or emission band shapes.[5a,b,d,39] These studies reported the temperature dependence of λ_s in weak and mildly polar solvents. Both continuum and molecular theories

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TABLE 4: Solvent Reorganization Energy and the Solvation Component of the Equilibrium Free Energy Gap (eV) at $T_0 = 300$ K: Dissection into Contributions from Permanent (Subscript "p") and Induced (Subscript "ind") Dipoles. Each Component is also Split into the Orientational and Density Contributions

λ_p			λ_{ind}			$T(\partial\lambda_p/\partial T)_P$, eV			$T(\partial\lambda_{ind}/\partial T)_P$, eV		
or.	dens	total	or.	dens	total	or.	dens	total	or.	dens	total
0.45	0.15	0.60	0.007	0.013	0.02	−0.05	-0.10	−0.15	−0.01	−0.03	−0.04

$-\Delta F_p$			$-\Delta F_{ind}$			$T(\partial\Delta F_p/\partial T)_P$, eV			$T(\partial\Delta F_{ind}/\partial T)_P$, eV		
or.	dens	total	or.	dens	total	or.	dens	total	or.	dens	total
0.81	0.28	1.09	0.008	0.012	0.02	0.13	0.20	0.33	0.01	0.03	0.04

predict a negative temperature dependence of λ_s in such solvents. A decrease of the Stokes shift with increasing temperature was reported by Ma et al.[40] for a nonpolar solute in the strongly polar solvent propylene carbonate. In contrast to this report, no significant temperature dependence of λ_s was found in highly polar solvents for outersphere ET in multiply charged, mixed-valence complexes.[41] The temperature independence of λ_s in the mixed-valence complexes may be a compensatory effect of the ionic electrolyte atmosphere. The electrolyte concentration is known to produce a substantial effect on ET activation parameters for such ET systems.[42]

In an effort to gain more insight into the origin of solvent reorganization in polar solvents, two different dissections of the solvent reorganization energy have been employed in this paper. The first approach effected separation according to the nature of the solute-solvent interaction potential: λ_s was divided into components from permanent λ_p and induced λ_{ind} dipoles (eq 22). The second approach partitions λ_s according to the nature of the solvent modes contributing to the ET activation: λ_s was divided into one component arising from orientational fluctuations of the permanent and induced dipoles λ_s^{or} and a second component arising from dipoles translations λ_s^{dens} (eq 47). ET activation in the continuum model arises from orientational fluctuations of the solvent permanent dipoles and does not include contributions from induced dipoles and dipole translations.[12c,26] Thus, both dissections of λ_s include one component present in the continuum model (λ_p or λ_s^{or}) and one component that is unique to the molecular description of the solvent (λ_{ind} or λ_s^{dens}).

The magnitudes and temperature derivatives of the λ_s components arising from the different analyses are summarized in Tables 3 and 4. The present analyses support the traditional view that solvent activation of ET arises principally from thermal motions resulting in changes of the coordinates of permanent (noninduced) partial charges on the solvent molecules. The induction reorganization produces a minor contribution to both the reorganization energy and its temperature dependence (Table 4). At 300 K, reorientation of the solvent permanent dipoles is the principal source of the solvent reorganization energy and of the solvation energy ΔF_s (Table 4). However, the present analysis clearly demonstrates that *molecular translation of the solvent permanent dipoles is the principal source of temperature dependence for both the solvent reorganization energy and the solvation free energy in acetonitrile.* Whereas the contribution of the total density reorganization λ_s^{dens} is about one-third as large as λ_s^{or}, the temperature coefficient $(\partial\lambda_s^{dens}/\partial T)_P$ is twice as large as the temperature coefficient $(\partial\lambda_s^{or}/\partial T)_P$. The two solvent modes thus play complementary roles in the solvent's total response: rotations mainly contribute to the energy of solvation and translational solvent modes are chiefly responsible for the entropic part of the solvent response, quantified here as temperature slope of the Stokes shift.

Very similar behavior was theoretically predicted for intermolecular ET between widely separated donor and acceptor units.[12a,b] This similarity suggests that density reorganization should induce an overall negative temperature dependence of the solvent reorganization energy in polar solvents for both intramolecular and intermolecular electron transfer reactions. The magnitude of this negative temperature dependence should vary slightly for the two ET configurations as the molecular model predicts opposite signs for $(\partial\lambda_s^{or}/\partial T)_P$: slightly negative for intramolecular ET (Table 3), positive for intermolecular reactions.[12a,b] This difference arises from the topology of the charge distributions: spherically symmetric for intermolecular ET and dipolar for intramolecular ET. In the latter case, the transverse component of the solvent polarization response produces a small negative temperature dependence of the orientational reorganization energy.[12c] The transverse component of the solvent polarization response is negligible for widely separated donor and acceptor groups (i.e., for intermolecular ET). Thus, these models lead to the prediction that the temperature slope of the solvent reorganization energy should become *less* negative with increasing separation of the donor and acceptor moieties.[43]

The different temperature dependences of the orientational and density reorganization arise from the different lengthscales of the corresponding solvent fluctuations: macroscopic, long-ranged for orientational fluctuations and microscopic, short-ranged for density fluctuations.[12] The connection between the language of reorganization free energies and energetics of solvent fluctuations is provided by the following equation[9b,10b,11e]

$$\lambda_s = (1/2k_B T)\langle(\delta\Delta E)^2\rangle \tag{48}$$

It relates the solvent reorganization energy to the mean-squared fluctuation (second cumulant) $\langle(\delta\Delta E)^2\rangle$. The instantaneous energies E_i in eq 11 include the additive solute−solvent interaction energy $e_i(0j)$

$$E_i = U_{ss} + I_i + \sum_j e_i(0j) \tag{49}$$

that leads to splitting of the second cumulant into the sum of two contributions

$$\langle(\delta\Delta E)^2\rangle = \langle(\delta\Delta E)^2\rangle_1 + \langle(\delta\Delta E)^2\rangle_2 \tag{50}$$

The one-solvent response

$$\langle(\delta\Delta E)^2\rangle_1 = N\langle(\delta\Delta e(01))^2\rangle \tag{51}$$

arises from fluctuations of a single solvent molecule "1" (N is the number of the solvent molecules). The two-solvent response

$$\langle(\delta\Delta E)^2\rangle_2 = N(N-1)\langle\delta\Delta e(01)\delta\Delta e(02)\rangle \tag{52}$$

originates in correlated fluctuations of two different solvent molecules "1" and "2".

In order to obtain the solvent reorganization energy arising from the permanent dipoles we need to use the differential solute−solvent dipole−dipole potential $\Delta\mathbf{m}_{0i}\cdot\mathbf{u}_p$ (see eq 7) instead of Δe in eqs 51 and 52. The two components $\langle(\delta\Delta E)^2\rangle_1^{\text{or}}$ and $\langle(\delta\Delta E)^2\rangle_2^{\text{or}}$ arising from orientational fluctuations of the permanent dipoles are very close in absolute magnitude and have opposite sign as a consequence of quasi-macroscopic character of these fluctuations. For an intermolecular ET configuration, these components are expressed as[12]

$$\langle(\delta\Delta E)^2\rangle_1^{\text{or}} = 6k_BTy_0q^2\lambda_0$$

$$\langle(\delta\Delta E)^2\rangle_2^{\text{or}} = -6k_BTy_0q^2\lambda_0\left(1 - \frac{\epsilon_s - \epsilon_\infty}{3y_0q^2\epsilon_s\epsilon_\infty}\right) \quad (53)$$

where

$$\lambda_0 = (1/8\pi)\int\Delta D(\mathbf{r})^2 d\mathbf{r} \quad (54)$$

is the vacuum electrostatic energy corresponding to the difference of the electric displacements $\Delta D(\mathbf{r})$ for the solute in the final and initial ET states; y_0 is given by eq 43 and $q = (\epsilon_\infty + 2)/3\epsilon_\infty$. Extensive cancelations between the terms for $\langle(\delta\Delta E)^2\rangle_1^{\text{or}}$ and $\langle(\delta\Delta E)^2\rangle_2^{\text{or}}$ eliminates the explicit dependence on temperature and reproduces the usual Marcus−Hush relationship for the solvent reorganization energy in strongly polar fluids.[44] The density component of the solvent reorganization energy is also proportional to k_BTy_0.[12a−c] However, a cancelation between the one-solvent and two-solvent response terms does not occur for λ_s^{dens} because the two-solvent response term is substantially smaller than the one-solvent term. The factor k_BT therefore cancels $1/k_BT$ in y_0, and the density component of the second cumulant does not contain an explicit dependence on temperature. Substitution into eq 48 produces an explicit $1/T$ dependence of the density reorganization. The same is true for the component of the solvent reorganization due to induction forces: λ_{ind} in eqs 24 and 38 is proportional to $1/T$. The temperature dependence thus discriminates between the localized and delocalized collective solvent modes.

As is seen from eq 48, fluctuations of orientational and density configurations of the solvent are responsible for a nonzero solvent reorganization energy. If we consider a solvent of molecules with fixed coordinates and allow only solvent orientations, we get the orientational reorganization energy. There is also an orientational component for the reorganization energy involving induced solvent dipoles. Although the induced dipoles orient instantaneously in an external field, the microscopic field in the liquid fluctuates continually producing fluctuations of the orientation of the induced molecular dipole. According to eq 48, this leads to an orientational component of the induction reorganization energy. This component is half as large as the density component arising from modulation of the solute-solvent induction potential by molecular translations (Table 4). Since fluctuations of the field of induced solvent dipoles should be relatively weak, induction reorganization is chiefly produced by density fluctuations. The opposite picture exists for reorganization by the permanent solvent dipoles (Table 4): the reorganization component due to permanent dipole reorientations is larger than that of dipole translations as rotations in dense liquids are less hindered than translations.[45]

The temperature slopes of the reorganization parameters represent entropic components of the corresponding Gibbs thermodynamic potentials. λ_s and ΔF_s can be written in terms
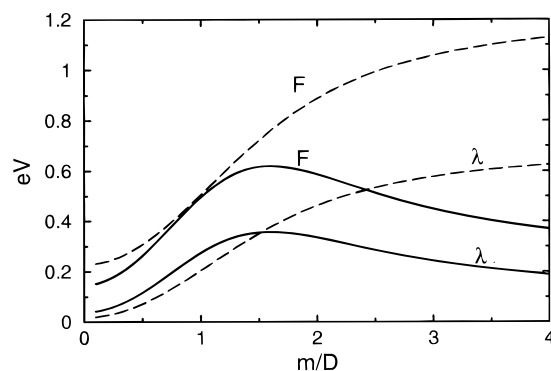

Figure 4. Calculated λ_s and $-\Delta F_s$ (dashed lines) and their entropic components, Ts_s^λ and $-Ts_s^F$ (solid lines) as a function of the solvent dipole moment. The labels λ and F refer to λ_s and ΔF_s, respectively. The other solvent parameters are those appropriate to acetonitrile (Table 2).

of enthalpy and entropy components

$$\lambda_s = h_s^\lambda - Ts_s^\lambda \qquad \text{and} \qquad \Delta F_s = h_s^F - Ts_s^F \quad (55)$$

where

$$s_s^\lambda = -\left(\frac{\partial\lambda_s}{\partial T}\right)_P \qquad \text{and} \qquad S_S^F = -\left(\frac{\partial\Delta F_s}{\partial T}\right)_P \quad (56)$$

The molecular model clearly predicts that the entropies s_s^λ and s_s^F are nonmonotonic functions of the solvent, permanent dipole moment. Figure 4 presents the dependence of Ts_s^λ, $-Ts_s^F$, λ_s, and $-\Delta F_s$ on the magnitude of the solvent dipole moment, with all other solvent parameters characteristic of acetonitrile. A maximum temperature dependence of λ_s and $-\Delta F_s$ is predicted in weakly polar solvents, with $m \simeq 1.5$ D. Two previous studies of CT state thermochromism detected maximum temperature dependence of the Stokes shift in solvents with $m \simeq 1.2$ D, although the solvents investigated differed by more than just the solvent dipole moments.[5b,46] For solvent dipoles $m \leq 1.5$ D the entropies and free energies are approximately equal[47]

$$\lambda_s \simeq Ts_s^\lambda \simeq h_s^\lambda/2, \quad \Delta F_s \simeq Ts_s^F \simeq h_s^F/2 \quad (57)$$

Equation 57 can be used to approximate the entropic barrier of ET in weakly polar solvents.

The theoretical model employed in this paper was intentionally simplified to provide an easily interpretable picture of the solvation thermodynamics in intramolecular ET reactions. Nonetheless, it includes several important features of real solvents: (i) orientational fluctuations of the solvent permanent dipoles, (ii) translations of permanent dipoles, and (iii) translations of induced dipoles. Two assumptions need to be revised in order to extend the present model to a wider range of optical chromophores and solvents: (i) zero solvent quadrupole moment and (ii) state independent solute polarizability. The extension to include a variable solute polarizability is relatively straightforward.[24] Application to experimental results is, however, hampered by the scarcity of data on excited state polarizabilities for most optical chromophores. The inclusion of the solvent molecular quadrupole is necessary to extend the analysis to weakly polar solvents and this work is currently underway.[19]

The present paper gives the first experimental evidence of the theoretically predicted[12a−c] failure of continuum models to describe temperature derivatives of the solvent reorganization energy and, therefore, of the entropy component of the activation

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barrier of ET reactions. If this deficiency is general for continuum descriptions of solvation,[27c,48] continuum models should be used with caution for interpretation of activation entropies of chemical reactions involving changes in reactant multipole states.

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(37) The density and orientational contributions to the linear solvent response can be completely separated because they have different symmetries. As a result, there are no density/orientation cross terms in the perturbation expansions used here. Instantaneous normal mode analyses of computer simulations of solvation indicate participation of many different solvent modes, in the frequency domain. The resulting frequency spectrum does exhibit cross correlations of translational and rotational modes, but these are small in comparison to the pure translational and rotational components. Furthermore, the integrated cross term spectrum is identically zero indicating that cross terms make identically zero contribution to the equilibrium properties.[38a] Another manifestation of this effect is the zero value of the cross velocity time correlation function at $t = 0$.[38b] As far as the equilibrium response is concerned, rotational and translation modes are fully decoupled in the perturbation formalism and in more exact approaches.

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