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Free Energies of Electron Transfer Reactions in Polarizable, Nondipolar, Quadrupolar Solvents

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A continuum theory is developed for describing the influence of polarizable, nondipolar, quadrupolar solvents on charge-transfer processes. The fluctuating configuration of solvent quadrupole moments and associated nonequilibrium free energy are described in terms of multidimensional solvent coordinates. The solvent reorganization free energy is obtained in the framework of both one- and two-sphere cavity descriptions of the reaction systems. As an application, electron transfer for bridged donor−acceptor systems in benzene is considered. It is found that the continuum theory predictions for outer-sphere reorganization free energy are in good accord with both experimental estimates and molecular-level theory results.

Introduction

The reorganization of solvent dipole moments plays a major role in charge-transfer kinetics and related spectroscopy in solution. In the Marcus theory[1,2] of outer-sphere electron transfer (ET) reactions, the activation barrier height $\Delta G^{\ddagger}$ and solvent reorganization free energy ΔG_r are related by

$$\Delta G^{\ddagger} = \frac{1}{4\Delta G_r}(\Delta G_r + \Delta G_{rxn})^2 \tag{1}$$

where ΔG_{rxn} is the free energy of reaction. In eq 1, the electronic coupling relevant to ET is assumed to be weak, so that the reaction occurs nonadiabatically. In a dielectric continuum solvent description, ΔG_r can be approximated as[1,2]

$$\Delta G_r = (\Delta q)^2\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right)\left(\frac{1}{2R_D} + \frac{1}{2R_A} - \frac{1}{R}\right) \quad \text{(two-sphere cavity model)} \tag{2}$$

where R_D and R_A are the cavity radii for the donor and acceptor moieties, R is the separation between the two and Δq is the charge transferred. The optical and static dielectric constants, ϵ_∞ and ϵ_0, describe the response of the electronic and total polarizations of the solvent, respectively. The sister expression of eq 2 in the single-sphere cavity formulation is

$$\Delta G_r = \frac{3(\epsilon_0 - \epsilon_\infty)}{(2\epsilon_\infty + 1)(2\epsilon_0 + 1)}\frac{1}{a^3}(\Delta\mu)^2 \quad \text{(one-sphere cavity model)} \tag{3}$$

where a is the cavity size and $\Delta\mu$ is the dipole moment change associated with charge transfer, i.e., $\Delta\mu = \Delta q R$. Except for the uncertainties associated with cavities, eqs 2 and 3, together with eq 1, provide a very simple and yet clear and elegant framework to analyze and interpret ET free energetics and the related Stokes shift in polar solvents.

The status of ET theory for nondipolar, quadrupolar solvents, such as benzene and dense CO_2, is a rather different story. While there is convincing experimental evidence for the importance of the solvent quadrupole reorganization,[3−11] there is no corresponding theory with the simplicity and clarity of eqs 2 and 3. This is mainly due to the lack of theoretical attention paid to the construction of a continuum formulation for describing free energetics in these solvents. Earlier attempts with a local interaction description were mainly limited to the investigation of macroscopic liquid properties[12−14] and equilibrium solvation.[15] While several molecular-level approaches do capture reorganization aspects of these solvents,[16−19] their practicality is often overshadowed by the complexity of theory involved in the analyses.

Recently, we have developed a novel continuum theory to describe equilibrium and nonequilibrium solvation in nondipolar, quadrupolar solvents.[20,21] Unlike previous attempts, the effective Hamiltonian involves both local and nonlocal interactions that have a clear connection to molecular-level descriptions. Its application to equilibrium solvation shows that the polarity of quadrupolar solvents measured as their solvating power of localized solutes is much higher than that predicted by their dielectric constants.[20] In this Letter, we apply this theory to study ET. Using a multipole expansion,[22] we obtain a free energy hypersurface in terms of multidimensional solvent coordinates,[23,24] which gauge the nonequilibrium solvent quadrupolar configurations. In this paper, we confine ourselves to outer-sphere reorganization free energetics. Further details and applications to other systems will be reported elsewhere.[21]

Formulation

We consider an ET reaction system—termed as a solute hereafter—immersed in a spherical cavity of radius a in a polarizable, nondipolar, quadrupolar solvent. In this initial attempt, we do not distinguish between the induced and permanent components of the solvent quadrupole moments to simplify our formulation. In the continuum formalism,[25−27] the solvent is then described in terms of the densities of its quadrupole and induced dipole moments after a suitable averaging process.[28] Hereafter, these density variables will be referred to as quadrupolarization and electronic polarization fields, Q and $\mathbf{P}_{el}$, respectively. The effective Hamiltonian $\hat{H}$ for the combined solute−solvent system in the presence of arbitrary $\mathbf{P}_{el}$ and Q is[20,21]

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$$\begin{aligned}\hat{H} = \hat{H}^0 &+ \frac{1}{2\chi_{\rm el}}\int^V {\rm d}\boldsymbol{r}\, |\mathbf{P}_{\rm el}(\mathbf{r})|^2 \\ &+ \frac{1}{2}\int^V {\rm d}\boldsymbol{r} \int^V {\rm d}\boldsymbol{r}'\, \mathbf{P}_{\rm el}(\mathbf{r})\cdot\left[\nabla\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\cdot\mathbf{P}_{\rm el}(\mathbf{r}') \\ &- \int^V {\rm d}\boldsymbol{r}\, \mathbf{P}_{\rm el}(\mathbf{r})\cdot\hat{\mathcal{E}}(\mathbf{r}) + \frac{1}{6C_Q}\int^V {\rm d}\mathbf{r}\, Q(\mathbf{r}){:}Q(\mathbf{r}) \\ &+ \frac{1}{3}\int^V {\rm d}\boldsymbol{r} \int^V {\rm d}\boldsymbol{r}'\, \mathbf{P}_{\rm el}(\mathbf{r})\cdot\left[\nabla\nabla'\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]{:}Q(\mathbf{r}') \\ &+ \frac{1}{18}\int^V {\rm d}\boldsymbol{r} \int_{0^+}^V {\rm d}\boldsymbol{r}'\, Q(\mathbf{r}){:}\left[\nabla\nabla\nabla'\nabla'\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]{:}Q(\mathbf{r}') \\ &- \frac{1}{3}\int^V {\rm d}\boldsymbol{r}\, Q(\mathbf{r}){:}\nabla\hat{\mathcal{E}} \qquad (4)\end{aligned}$$

where $\hat{H}^0$ and $\hat{\mathcal{E}}$ are the solute electronic Hamiltonian and electric field operators in a vacuum, $\mathbf{r}$ and $\mathbf{r}'$ represent positions in the solvent medium, the superscript V indicates that the integrations are restricted to the volume outside the cavity, and $A{:}B$ for second-rank tensors A and B denotes $\Sigma_{ij}A_{ij}B_{ij}$. For simplicity, both the dipolar and quadrupolar susceptibilities, $\chi_{\rm el}$ and C_Q, are assumed to be scalars. The former is related to the optical dielectric constant by $\epsilon_\infty = 1 + 4\pi\chi_{\rm el}$. In eq 4 the trace part of the solvent quadrupolarization is retained, so that $Q(\mathbf{r})$ is the local density of the quadrupole moment q evaluated at $\mathbf{r}$

$$q \equiv \frac{3}{2}\int {\rm d}\mathbf{r}'\, \rho(\mathbf{r}+\mathbf{r}')\mathbf{r}'\mathbf{r}' \qquad (5)$$

with the charge distribution ρ.

Except for the terms involving Q, a Hamiltonian similar to $\hat{H}$ (plus the contribution of solvent orientational polarization) has been used extensively in solvation studies in dipolar solvents.[29] The four terms involving Q in eq 4 represent, in sequence, the free energy cost for inducing quadrupolarization, and continuum analogues of solvent dipole−quadrupole, quadrupole−quadrupole, and quadrupole−solute charge interactions. Since q does not interact with itself, the corresponding contribution at the continuum level, viz., interaction of $Q(\mathbf{r})$ and $Q(\mathbf{r}')$ at $\mathbf{r} = \mathbf{r}'$ should be excluded. This is denoted as the subscript 0^+ in eq 4. The subtraction of a similar self-interaction term for $\mathbf{P}_{\rm el}$ is absorbed into $\chi_{\rm el}$, for convenience. We parenthetically note that with a harmonic oscillator model for the solvent molecular polarizability,[30] this prescription of $\chi_{\rm el}$ leads to the well-known Lorenz−Lorentz relation.[31] This indicates that correlation between the charge distributions of different solvent molecules is not reflected in our continuum theory.[31] We also point out that explicit spatial dispersions, e.g., $(\nabla\cdot\mathbf{P}_{\rm el})^2$ and $(\nabla\cdot Q)^2$, are ignored in our formulation.

As detailed in ref 32, the relative time scales of the solute and solvent electronic motions play an important role in ET free energetics. In this Letter we restrict our consideration to weakly coupled ET, where the solvent electronic response is much faster than the transferring solute electron. We can then eliminate $\mathbf{P}_{\rm el}$ adiabatically through $\delta\hat{H}/\delta\mathbf{P}_{\rm el} = 0$ because it always follows the localized solute charge distributions during ET.[22,32] To incorporate this, we first simplify the representations of the field variables as[20,21]

$$\mathbf{P}_{\rm el}(\mathbf{r}) = -\nabla\Lambda_{\rm el}(\mathbf{r}) \qquad Q(\mathbf{r}) = -3[\nabla\nabla\Lambda_Q(\mathbf{r}) + \mathbf{I}f(\mathbf{r})] \quad (6)$$

where $\Lambda_{\rm el}$, Λ_Q, and f are scalar functions and $\mathbf{I}$ is the unit matrix. Because of cavity boundaries, however, the adiabatic elimination of $\mathbf{P}_{\rm el}$ in this scalar representation is still a formidable task. To efficiently handle this, we borrow the solvent coordinate description, widely used for dipolar solvents.[22−24] To be specific, we extend the multipole expansion of equilibrium Q in ref 20 to a general nonequilibrium configuration as[33]

$$\Lambda_Q(\mathbf{r}) = \frac{C_Q}{3\epsilon_\infty}\sum_{lm}\sqrt{\frac{4\pi}{2l+1}}S_l^{-1}\left[\frac{1}{r^{l+1}} + \kappa^{l+1}\beta_l k_l(\kappa r)\right]\lambda_{lm}Y_{lm}(\theta,\phi)$$

$$f(\mathbf{r}) = -\frac{16\pi\kappa^4 C_Q^{\ 2}}{315\epsilon_\infty}\sum_{lm}\sqrt{\frac{4\pi}{2l+1}}S_l^{-1}\kappa^{l+1}\beta_l k_l(\kappa r)\lambda_{lm}Y_{lm}(\theta,\phi) \quad (7)$$

where Y_{lm} are spherical harmonics and the origin of the coordinate system is at the center of the solute molecule. Here λ_{lm} represents the lm-multipole component of a hypothetical solute charge distribution, with which the nonequilibrium Q under consideration would be in equilibrium. In eq 7, β_l and S_l are dimensionless quantities defined as[20,21]

$$\beta_l = \left[\frac{l+1}{2l+1}k_{l+1}^d(\kappa a) + \frac{l}{2l+1}k_{l-1}^d(\kappa a) + \frac{16\pi}{105}\kappa^2 C_Q k_l(\kappa a)\right]^{-1}\frac{(l+1)(l+2)}{(\kappa a)^{l+3}}$$

$$S_l = 1 + \frac{l}{(2l+1)\epsilon_\infty}\left[1 - \epsilon_\infty + \frac{4\pi}{3}(l-1)\kappa^2 C_Q(\kappa a)^l\beta_l k_{l-1}(\kappa a) + \left(1 - \frac{16\pi}{35}\kappa^2 C_Q\right)(\kappa a)^{l+1}\beta_l k_l(\kappa a)\right] \quad (8)$$

and $k_l(z)$ and $k_l^d(z)$ are related to modified Bessel functions $K_n(z)$

$$k_l(z) = \sqrt{\frac{2}{\pi z}}K_{l+1/2}(z) \qquad k_l^d(z) = \frac{l}{z}k_l(z) - k_{l+1}(z) \quad (9)$$

The lengthy expression in square brackets on the right-hand side of S_l arises from the cavity boundary.[20,21] The κ factor in eqs 7 and 8 determined by

$$\kappa^2 C_Q = \frac{3}{32\pi}[(35 - 12\eta) + \sqrt{1225 - 280\eta + 144\eta^2}]$$

$$\eta = \left(1 - \frac{1}{\epsilon_\infty}\right)^{-1} \quad (10)$$

measures the degree of screening of the solute electric field by Q.

After some algebra we can eliminate $\mathbf{P}_{\rm el}$ and obtain $\hat{H}$ in terms of arbitrary λ_{lm} (and thus Q)[21]

$$\hat{H} = \hat{H}^0 - \frac{1}{2}\sum_{lm}R_\infty^{lm}\hat{\varphi}_{lm}^{\ 2} + \frac{1}{2}\sum_{lm}R_Q^{lm}\,(\lambda_{lm}^{\ 2} - 2\lambda_{lm}\hat{\varphi}_{lm}) \quad (11)$$

where $\hat{\varphi}_{lm}$ is the solute lm-multipole operator

$$\hat{\varphi}_{lm} = \sqrt{\frac{4\pi}{2l+1}}\int {\rm d}\mathbf{x}\, x^l Y_{lm}^*(\theta_x,\phi_x)\,\hat{\rho}_{\rm ET}(\mathbf{x}) \quad (12)$$

associated with its charge density operator $\hat{\rho}_{\rm ET}(\mathbf{x})$. The reaction field factors R_∞^{lm} and R_Q^{lm} in eq 11

$$R_{\infty}^{lm} = \frac{(l+1)(\epsilon_{\infty}-1)}{(l+1)\epsilon_{\infty}-l}\frac{1}{a^{2l+1}}$$

$$R_{Q}^{lm} = \frac{4\pi(l+1)(l+2)(2l+1)}{3\epsilon_{\infty}[(l+1)\epsilon_{\infty}+l]}\frac{\kappa^2 C_Q}{S_l}F_l(\kappa a)\frac{1}{a^{2l+1}} \quad (13)$$

characterize strengths of $\mathbf{P}_{\text{el}}$ and Q responses to the lm-multipole moment, respectively. The main difference between R_{∞}^{lm} and R_{Q}^{lm} is the $F_l(\kappa a)$ factor in the latter

$$F_l(y) \equiv \frac{1}{y^2} + \frac{y^l}{2l+1}\beta_l(y)k_{l+1}(y) = \frac{\zeta(2l+1)yk_l(y) - l(l-1)k_{l-1}(y)}{y^2[(l+1)(l+2)k_{l+1}(y) + \zeta(2l+1)yk_l(y) - l(l-1)k_{l-1}(y)]}$$

$$\zeta \equiv 1 - \frac{16\pi}{105}\kappa^2 C_Q \quad (14)$$

which gauges the short-range effect of the solute-quadrupole interactions, compared to solute-dipole interactions (see Figure 1). The term involving R_{∞}^{lm} on the right-hand side of eq 11 describes the dispersion and polarization stabilizations of the solute through Coulombic interactions with $\mathbf{P}_{\text{el}}$.[22] The terms quadratic and linear in λ_{lm} represent, respectively, the self-energy of Q and its interaction with the solute, screened by $\mathbf{P}_{\text{el}}$. We note that except for the difference arising from the R_{Q}^{lm} factor, the basic structure of eq 11 is exactly the same as that of $\hat{H}$ developed in ref 22 for polarizable, dipolar solvents. Thus, the analysis of solvent polarization fluctuations there is nearly directly transferable to the present case.

Before we turn to ET, we briefly pause here for perspective. At equilibrium, our formulation based on eq 4 yields a nonlocal constitutive relation $\mathbf{D}(\mathbf{k}) = \epsilon(\mathbf{k})\cdot\mathbf{E}(\mathbf{k})$ with the neglect of the boundaries.[21] Here $\mathbf{k}$ is a wave vector, $\mathbf{D}$ and $\mathbf{E}$ are the electric displacement vector and Maxwell field, related in $\mathbf{r}$-space via[21,25-27]

$$\mathbf{D} = \mathbf{E} + 4\pi[\mathbf{P}_{\text{el}} - (^1/_3)\nabla\cdot Q] \quad (15)$$

and $\epsilon(\mathbf{k})$ is the nonlocal dielectric permittivity tensor,[34] which depends parametrically on the susceptibilities χ_{el} and C_Q in eq 4. While this formulation couched in $\epsilon(\mathbf{k})$ and its nonequilibrium extensions provide a convenient macroscopic description for a bulk medium, the incorporation of the cavity effects in the calculation of the local solvent field and its interaction with the solute is not straightforward in the $\mathbf{k}$-space representation. This is mainly due to the complication arising from the boundaries, coupled with the nonlocal nature of the theory. By contrast, the explicit separation of $\mathbf{P}_{\text{el}}$ and Q employed here allows a systematic analysis of nonequilibrium solvation in $\mathbf{r}$-space with account of the cavity effects.[21]

Nonadiabatic Electron-Transfer Reactions

We now consider nonadiabatic ET using eq 11. Since microscopic variables are projected out through statistical averaging in $\hat{H}$ there, its expectation value yields the system free energy.[1] Thus, in the multidimensional solvent coordinate system spanned by λ_{lm}, the diabatic free energy hypersurfaces, G_{R} and G_{P}, for the ET reactant (R) and product (P) states are defined by

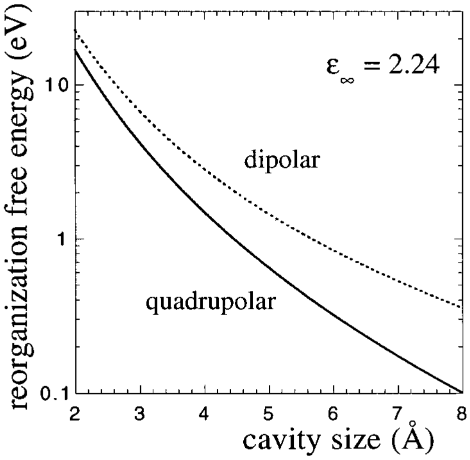

Figure 1. ΔG_{r} as a function of cavity size: quadrupolar benzene with $C_Q = 3.56$ Å^2 (—); model dipolar solvent with $\epsilon_0 = 35$ (···). For both solvents, $\epsilon_{\infty} = 2.24$ (corresponding to the benzene value) and $\Delta\mu = 34$ D are employed. The latter is the estimated dipole moment change for the bridged donor−acceptor systems studied in ref 8.

$$G_{\text{R,P}}[\lambda_{lm}] = \langle\psi_{\text{R,P}}|\hat{H}^0|\psi_{\text{R,P}}\rangle - \frac{1}{2}\sum_{lm}R_{\infty}^{lm}\langle\psi_{\text{R,P}}|\hat{\varphi}_{lm}{}^2|\psi_{\text{R,P}}\rangle + \frac{1}{2}\sum_{lm}R_{Q}^{lm}\{\lambda_{lm}{}^2 - 2\lambda_{lm}\langle\psi_{\text{R,P}}|\hat{\varphi}_{lm}|\psi_{\text{R,P}}\rangle\} \quad (16)$$

where $\psi_{\text{R,P}}$ are the solute electronic wave functions associated with the R and P states. The respective minimum points on these surfaces given by

$$\lambda_{lm}^{\text{R,P}} = \langle\psi_{\text{R,P}}|\hat{\varphi}_{lm}|\psi_{\text{R,P}}\rangle \quad (17)$$

correspond to the stable Q configurations associated with the R and P states. The reorganization free energy ΔG_{r} for Q rearrangement is then

$$\Delta G_{\text{r}} = G_{\text{R}}[\lambda_{lm}^{\text{P}}] - G_{\text{R}}[\lambda_{lm}^{\text{R}}] = G_{\text{P}}[\lambda_{lm}^{\text{R}}] - G_{\text{P}}[\lambda_{lm}^{\text{P}}] = \frac{1}{2}\sum_{lm}R_{Q}^{lm}\{\langle\psi_{\text{P}}|\hat{\varphi}_{lm}|\psi_{\text{P}}\rangle - \langle\psi_{\text{R}}|\hat{\varphi}_{lm}|\psi_{\text{R}}\rangle\}^2 \quad (18)$$

In the simple dipole description of the solute charge distribution, ΔG_{r} reduces to

$$\Delta G_{\text{r}} = \frac{1}{2}R_{Q}^{lm}(\Delta\mu)^2 = \frac{36\pi\kappa^2 C_Q}{(2\epsilon_{\infty}+1)^2}F_1(y)\left[1 - \frac{6F_1(y)}{2\epsilon_{\infty}+1}\right]^{-1}\frac{(\Delta\mu)^2}{a^3} \approx \frac{36\pi\kappa^2 C_Q}{(2\epsilon_{\infty}+1)^2}\left\{\frac{\zeta(y+1)}{\zeta y^3 + (\zeta+2)y^2 + 6y + 6}\right\}\frac{(\Delta\mu)^2}{a^3} \quad (19)$$

where $y = \kappa a$ is a dimensionless cavity radius and the $F_1(y)$ term in the square brackets is neglected in passage to the final expression. It should be noticed that compared to the dipolar solvent eq 3, the only additional information needed for ΔG_{r} is the quadrupolar susceptibility C_Q (cf. eqs 10 and 14). In view of the lack of direct experimental information as well as the approximate nature of the continuum approach, we have proposed to determine C_Q spectroscopically in ref 20. To be specific, C_Q is chosen such that resulting $2\Delta G_{\text{r}}$ reproduces Stoke shift of coumarin 153, studied in ref 10. With $\epsilon_{\infty} = 2.24$, this yields $C_Q = 3.56$ Å^2 (and $\kappa = 0.633$ Å^{-1}) for benzene at room temperature. In the numerical calculations of ET in benzene below, this C_Q value is employed.

In Figure 1, the reorganization free energy of benzene calculated with eq 19 is shown as a function of a. We used $\Delta\mu = 34$ D to make contact with ref 8, where the bridged ET systems between the dimethoxyanthracene donor and cyclobutene dicarboxylate acceptor units were studied. For comparison, ΔG_r (eq 3) of a highly dipolar solvent with $\epsilon_0 = 35$ and $\epsilon_\infty = 2.24$ is also exhibited. ΔG_r for benzene decreases more rapidly with a than that for the dipolar solvent, primarily due to the first $F_1(y)$ term in eq 19. As mentioned above, this trend is closely related to the fact that the interactions involving quadrupoles are of shorter range than those involving dipoles. Despite this, the quadrupolar reorganization free energy remains quite substantial even for large a. With $a = 7.25$ Å employed in ref 8b for the above ET systems, our theory predicts $\Delta G_r \sim 0.15$ eV.[35] This compares well with the molecular-level estimate, 0.16 eV, there with the thermodynamic perturbation theory.[19]

Finally, we turn to ΔG_r in the presence of two spherical cavities. Its derivation à la Marcus is more involved than eq 19 because of the technical difficulty in extending $Q(\mathbf{r})$ to the origin where there is a singularity. The reason for this is that eq 7 is based on the equilibrium quadrupolarization configuration,[20] determined variationally outside the cavity.[33] With the removal of this anomaly at the singularity,[21] we find

$$\Delta G_r \approx \frac{4\pi\kappa^2 C_Q}{3{\epsilon_\infty}^2}(\Delta q)^2\left\{F_0(\kappa R_D)\frac{1}{R_D} + F_0(\kappa R_A)\frac{1}{R_A} - \zeta\frac{e^{-\kappa R}}{R}\right\}$$

$$= \zeta\frac{4\pi\kappa^2 C_Q}{3{\epsilon_\infty}^2}(\Delta q)^2\left\{\frac{1}{(\zeta {y_D}^2 + 2y_D + 2)R_D} + \frac{1}{(\zeta {y_A}^2 + 2y_A + 2)R_A} - \frac{e^{-\kappa R}}{R}\right\} \quad (20)$$

with $y_{D,A} = \kappa R_{D,A}$. The exponential factor $e^{-\kappa R}$ in the solvent-mediated donor−acceptor interaction clearly reveals the short-range character of the quadrupolarization. As an application of eq 20, we briefly consider photoinduced ET of bridged porphyrin-quinone systems, studied by Mataga and co-workers.[7] They found that total reorganization free energy, i.e., inner sphere + outer sphere, in the nonadiabatic ET scheme is ∼0.8 eV in benzene. By fitting both charge separation and recombination kinetics data, they estimated that the outer-sphere contribution would be $\Delta G_r \approx 0.18$ eV although a larger value would yield a better agreement with the former data. With the cavity radii of 5 and 3.5 Å used in ref 7 for porphyrin and quinone, we assess $\Delta G_r \sim 0.29$ eV from eq 20. Considering the uncertainties in experimental estimates, this result seems to be in reasonable accord with ref 7.

In summary, we have developed a continuum theory to describe equilibrium and nonequilibrium solvation in polarizable, nondipolar, quadrupolar solvents. We have derived a simple expression for solvent reorganization free energy, couched in terms of cavity size, optical dielectric constant and quadrupolar susceptibility. Its application to electron-transfer reactions for various bridged donor−acceptor systems in benzene has yielded reasonable agreement with both experiments and molecular-level theories. This seems to indicate that the current theory correctly captures the essential features of nonequilibrium solvation in quadrupolar solvents. Nevertheless, it would be desirable to consider other charge shift systems to further test the theory. Also it would be worthwhile in the future to extend it to incorporate explicit spatial dispersions and separation of electronic and orientational quadrupolarizations.

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(33) Following ref 20, we neglect any oscillatory behavior that could be present in Q.

(34) For an earlier effort to determine $\epsilon(\mathbf{k})$ for quadrupolar solvents in the continuum framework, see ref 26. For molecular-level investigations, see refs 17 and 18b.

(35) For perspective, we point out that if we instead adopt the two-sphere cavity formulation in eq 20 below, we obtain $\Delta G_r \approx 0.3$ eV with the radius of ∼4 Å for both cavities.