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Optical Electron Transfer in Mixed Solvents. Major Energetic Effects from Unsymmetrical Secondary Coordination

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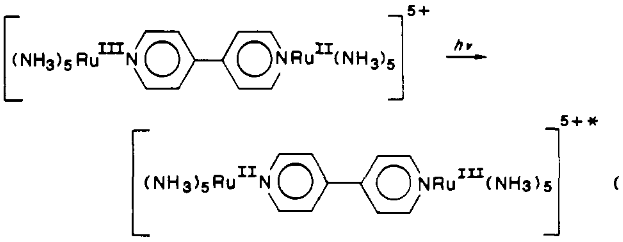
Optical electron transfer in the symmetrical, mixed-valence dimer $[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+}$ (4,4′-bpy is 4,4′-bipyridine) has been examined in mixtures of acetonitrile and dimethyl sulfoxide (Me_2SO) as solvent. From spectral and electrochemical measurements evidence was found for strong selective solvation by Me_2SO. For the metal-to-metal charge-transfer transition, unexpectedly large energetic effects were observed for the Me_2SO mole fraction range between 0 and ~0.1. The energetic effects were found to result from unsymmetrical secondary coordination for $(NH_3)_5Ru^{III}$ vs. $(NH_3)_5Ru^{II}$. The appearance of such effects suggests the existence of parallel rate effects for related thermal self-exchanges.

Introduction

We are initiating a program to study electron-transfer events in mixed solvents. Our focus is on optical electron transfer, especially involving molecules known to engage in strong specific interactions with the surrounding solvent. A substantial number of studies have preceded ours, focusing for the most part on rate measurements for homogeneous or heterogeneous (electrochemical) thermal electron transfer.[1-20] Unfortunately, despite the preponderance of effort in redox studies, relatively little has emerged of a fundamental nature. (In contrast, in other areas such as the kinetics of ligand substitution processes[21] and the thermodynamics of metal ion solvation[22] excellent progress has been made in understanding mixed-solvent phenomena.)

In our view the lack of progress in the electron-transfer area is understandable. Rates are complex quantities that can respond in a myriad of ways to solvent composition, and clearly their interpretation can be difficult. Studies of optical electron transfer appear to offer a solution to such difficulties: Franck–Condon factors, thermodynamic effects, and electronic coupling terms can each be extracted as separate pieces of information, and in covalently linked systems the estimation of precursor and successor stabilities is not a consideration.[23]

As an initial system we have selected the symmetrical dimer $[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+}$ in CH_3CN and dimethyl sulfoxide (Me_2SO) solvent mixtures (4,4′-bpy is 4,4′-bipyridine). The mixed-valence properties of this dimer are well established in pure solvents;[24,25] the properties of related monomers have likewise been extensively investigated.[26] We report here that for optical electron transfer within the dimer (eq 1) in mixed solvents



(1)

unexpectedly large energetic effects exist. Their appearance, however, can be accounted for in a quantitative fashion by considering the effects of unsymmetrical secondary coordination.

Experimental Section

Metal Complexes. $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5](PF_6)_4$, $[(NH_3)_5Ru(dmapy)](PF_6)_2$ (dmapy is (dimethylamino)pyridine), and $[(NH_3)_5Ru(dmabn)](PF_6)_2$ (dmabn is (dimethylamino)benzonitrile) were prepared by literature methods.[24a,26] Monomeric Ru(III) complexes were prepared in situ from the Ru(II) species by using Br_2 vapor as the oxidant. (This process consisted simply of adding an excess of the oxidant by syringe to the atmosphere above the solution in a stoppered cuvette and then mixing.) The mixed-valence form of the dimer (5+) was prepared (as a solid) from the 6+ and 4+ forms.

Measurements. Electrochemical measurements were made in a simple one-compartment cell (ca. 3 mL) using platinum working (0.12 cm^2 disk) and counter (wire) electrodes as well as a platinum wire pseudo-reference electrode. Half-wave potentials for the $[(NH_3)_5Ru(4,4'\text{-bpy})Ru$-

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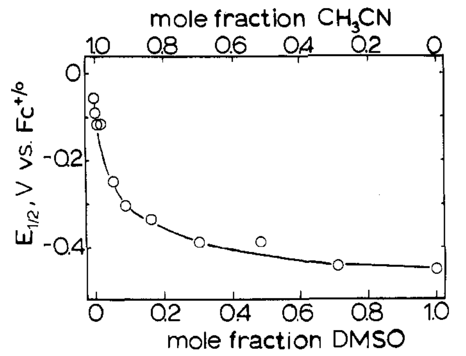


Figure 1. $E_{1/2}$ values for $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{6+/4+}$ vs. ferrocenium/ferrocene as a function of solvent composition in Me_2SO + CH_3CN. The supporting electrolyte is 0.02 M KPF_6.

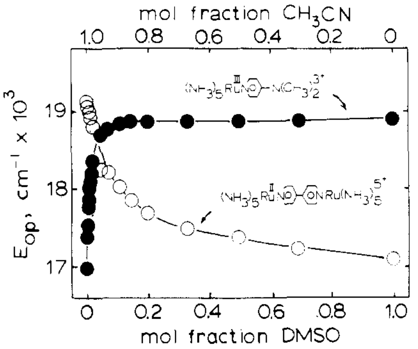


Figure 2. Transition energies: (O) metal-to-ligand charge transfer for $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{5+}$; (●) ligand-to-metal charge transfer for $[(NH_3)_5Ru(dmapy)]^{3+}$, in CH_3CN + Me_2SO mixtures.

$(NH_3)_5]^{6+/4+}$ couple were obtained by cyclic voltammetry, typically at 100 mV/s, by using a PAR 174A polarographic analyzer and a Houston Omnigraphics X-Y recorder. Waves for the 6+/5+ and 5+/4+ couples were too closely spaced to be resolved separately. To avoid complications from liquid-junction potentials, $E_{1/2}$ values were measured vs. an internal redox reference, $Ru(bpy)_3^{2+/+}$, and then converted to the ferrocenium/ferrocene ($Fc^{+/0}$) scale.[27] (Direct measurements against the $Fc^{+/0}$ couple were precluded due to interference with the couple of interest.) Due to dimer solubility problems in CH_3CN the concentration of the supporting electrolyte (KPF_6) was limited to 0.02 M.

Visible spectra, as well as near-IR spectra, were obtained with a Perkin-Elmer 330 spectrophotometer. Additional near-IR spectra were gathered with a Cary 17 spectrophotometer. All were corrected for residual absorbances by the solvent.

Results and Discussion

Half-wave potentials for the dimeric couple $[(NH_3)_5Ru(4,4'\text{-bpy})Ru(NH_3)_5]^{6+/4+}$ vs. ferrocenium/ferrocene are shown in Figure 1 as a function of solvent composition. The shift in potential between pure acetonitrile and pure Me_2SO is large, but is consistent with observations for related pentaammine monomers.[28] A more striking result is the sharp decline in potential with relatively small additions of Me_2SO. At a mole fraction (m_{Me_2SO}) of 0.2, for example, the $E_{1/2}$ is nearly as negative as in pure Me_2SO. We interpret this result as strong evidence for selective solvation by Me_2SO. Consistent with previous reports,[26,29] the basis of the effect appears to be in specific donor–acceptor interactions between the acidic hydrogens of the coordinated ammonia ligands and basic functionalities of discrete solvent molecules. It is important to note that from the available (empirical) solvent scales, Me_2SO is a much stronger Lewis base than CH_3CN.[30]

Figure 2 illustrates the effect of solvent composition upon the energy of the metal to bridging ligand charge-transfer (MLCT) transition (eq 2) in the mixed-valence dimer. A similar result was obtained with the fully reduced dimer.

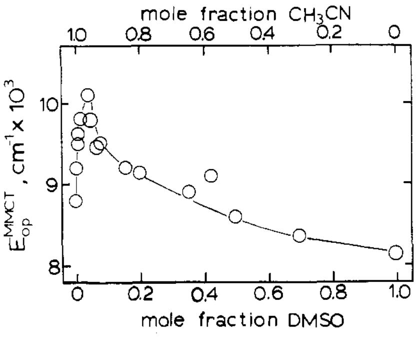
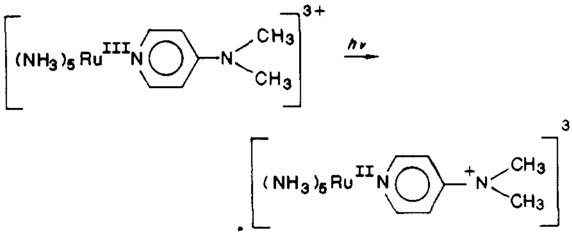


Figure 3. Optical electron transfer energies for $[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+}$ as a function of solvent composition in CH_3CN + Me_2SO mixtures.

$$[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+} \xrightarrow{h\nu} [(NH_3)_5Ru^{III}(4,4'\text{-bpy}^{\bullet -})Ru^{III}(NH_3)_5]^{5+*} \quad (2)$$

Direct assessment of the corresponding ligand-to-metal charge-transfer energy (E^{LMCT}) proved impossible in both the 5+ and 6+ dimers, due to overlap with ligand-based $\pi \rightarrow \pi^*$ transitions. Shown in Figure 2, as a surrogate for the dimer, is the solvent dependence of E^{LMCT} (eq 3) in the monomeric complex



(3)

$[(NH_3)_5Ru(dmapy)]^{3+}$. From the work of Curtis, Sullivan, and Meyer,[26] solvatochromic effects in these types of complexes are known to be dominated by interactions at the pentaammineruthenium center, rather than at the π-donor site. Also it should be noted that very similar results were obtained with $[(NH_3)_5Ru^{III}(dmabn)]^{3+}$ as the surrogate. Thus, it is likely that the reaction in eq 3 will accurately mimic the transition occurring in the dimer.

Qualitatively the spectral results resemble those from the electrochemical experiment. Both spectral experiments show marked energy shifts with only small increments of Me_2SO. If we keep in mind that the optical transitions occur with frozen solvent coordinates, the experiments represent direct probes of *ground-state* solvation. On this basis the interaction of Me_2SO with $(NH_3)_5Ru^{III}$ is clearly much stronger than that with $(NH_3)_5Ru^{II}$. For example, from Figure 2, conversion of the secondary coordination sphere of Ru^{III} from CH_3CN to Me_2SO can be considered to be roughly 50% complete at $m_{Me_2SO} = 0.011$. For Ru^{II} this point is reached at $m_{Me_2SO} = 0.11$.

It is worth considering the origin of the solvent-induced energy shifts in more detail. E^{MLCT} (or more generally, E_{op}) can be written as a sum of contributions:

$$E_{op} = \Delta E + \chi_i + \chi_s \quad (4)$$

In eq 4, ΔE is the thermodynamic energy difference between vibrationally equilibrated electronic isomers,[31] χ_i is the Franck–Condon contribution from bond vibrations within the complex, and χ_s is the Franck–Condon contribution from collective motions of the solvent. For substitutionally inert complexes, ΔE and χ_s

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[31] For MLCT and MMCT transitions involving excitation of Ru^{II}, ΔE will include an additional contribution from $d\pi^5$ energy level splitting of Ru^{III} in the excited state, induced by spin–orbit coupling. (Kober, E. M.; Goldsby, K. A.; Narayan, D. N. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *105*, 4303 and ref 24b and 25).

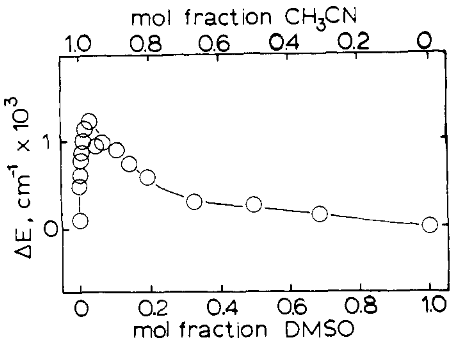

Figure 4. Redox asymmetry, ΔE, from unsymmetrical secondary solvation of $[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+}$ in CH_3CN + Me_2SO mixtures calculated from eq 6 and plotted vs. mole fraction.

are the terms most obviously dependent on solvent. Curtis et al. have shown[26] that for ammine complexes the thermodynamic term ΔE provides the predominant contribution to the solvent dependence of E^{MLCT}—a result that might also have been inferred from the strong solvent dependence of the $E_{1/2}$ of the Ru(III)/Ru(II) couple (Figure 1).

In Figure 3, band energies are plotted vs. solvent composition for optical electron transfer (or metal-to-metal charge transfer, MMCT) within the mixed-valence dimer, as in eq 1. The values in pure CH_3CN and pure Me_2SO are in good agreement with those obtained previously,[24] and between $m_{Me_2SO} = 0.5$ and 1.0 the energies are essentially those expected from mole fraction statistics. Between $m_{Me_2SO} = 0$ and ~0.1, however, a striking and unexpected feature appears. The transition energy increases sharply with increasing m_{Me_2SO}, peaking at $m_{Me_2SO} = 0.035 \pm 0.005$, some 1300 cm^{-1} above the value in pure acetonitrile. Further increases in Me_2SO lead to an initially sharp, but then more gradual, decrease in E^{MMCT}.

The appearance of such an effect is surprising given the well-defined and predictable behavior of the dimer in a series of pure solvents.[24,25] A careful analysis reveals that the effect is consistent with the available theory of optical electron transfer, but points to a fundamental difference between mixed and pure solvents. To understand this, we employ eq 4. In the MMCT experiment χ_i is presumably constant, but χ_s clearly changes with solvent composition.[23a] From Hush's treatment of optical electron transfer, χ_s should vary with $1/D_{op} - 1/D_s$, where D_{op} and D_s are the optical and static dielectric constants of the solvent.[23a] Values for D_{op} and D_s apparently are unavailable for CH_3CN + Me_2SO mixtures. For other mixtures, however, D_{op} and D_s typically vary in a monotonic and nearly linear fashion with solvent mole fraction.[32] In any case, sharp features such as the one found in Figure 4 are not encountered. This suggests that variations in χ_s cannot be the explanation for the unusual effects. In pure solvents, the remaining term (ΔE) is zero for electron transfer within symmetrical dimers because the electronic energy content of the reactant is identical with that of the vibrationally excited product (neglecting, for the moment, spin–orbit effects and ligand field asymmetry effects[31]).

The key difference in the mixed-solvent experiment is that optical excitation can lead to a redox isomer lying substantially higher in electronic energy ($\Delta E \neq 0$), on account of unsymmetrical secondary coordination by solvent:

$$x\mathrm{Me_2SO}\cdot[(NH_3)_5Ru^{III}(4,4'\text{-bpy})Ru^{II}(NH_3)_5]^{5+}\cdot y\mathrm{Me_2SO} \xrightarrow{h\nu} x\mathrm{Me_2SO}\cdot[(NH_3)_5Ru^{II}(4,4'\text{-bpy})Ru^{III}(NH_3)_5]^{5+*}\cdot y\mathrm{Me_2SO} \quad (5)$$

Equation 5 illustrates how the inherent symmetry of the optical transition (eq 1) is removed by selective solvation; in the electronic excited state, $(NH_3)_5Ru^{III}$ is trapped in the secondary coordination environment appropriate to $(NH_3)_5Ru^{II}$ (and vice versa). Equation 5 also indicates that the symmetry loss will be greatest when the fractional occupancies of the secondary coordination spheres by Me_2SO, designated by x and y, are most widely different. In terms of eq 4, the consequences are the appearance of a contribution to the redox asymmetry, ΔE, and an increase in E^{MMCT}. Note that in pure solvents, x equals y and ΔE is necessarily zero.

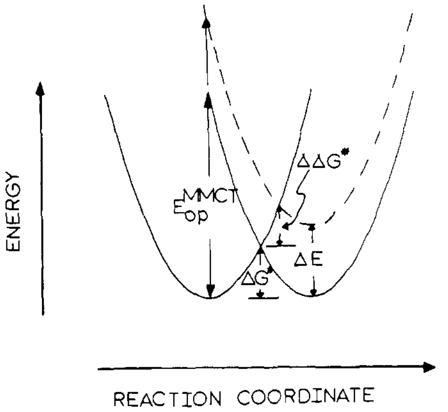

Figure 5. Schematic representation of the relationships among E^{MMCT}, ΔE, ΔG^*, and $\Delta\Delta G^*$.

To determine the energy costs for nonequilibrium secondary solvation we turn to Figure 2, and examine the dimer fragments separately. The plot of E^{LMCT} vs. mole fraction answers the first part of the question posed by eq 5: What is the cost of placing $(NH_3)_5Ru^{III}$ within the secondary (solvent) coordination sphere appropriate to $(NH_3)_5Ru^{II}$? The second part—the cost of placing $(NH_3)_5Ru^{II}$ in a secondary coordination sphere appropriate to $(NH_3)_5Ru^{III}$—is answered by the plot of E^{MLCT} vs. solvent composition. By combining E^{LMCT} and E^{MLCT}, we can obtain the overall energy cost. A correction needs to be made, however, for the fact that metal-to-ligand or ligand-to-metal charge transfer occurs, of course, at a nonzero energy even in pure solvents. We may write

$$\Delta E = E^{MLCT}(\text{mixed}) + E^{LMCT}(\text{mixed}) - E^{MLCT}(\text{pure}) - E^{LMCT}(\text{pure}) \quad (6)$$

where ΔE represents the redox asymmetry appearing in eq 5 due solely to unsymmetrical secondary coordination. It is important to note that the choice of pure solvent in eq 6 is unimportant, provided that it is the same for E^{LMCT} and E^{MLCT}. A second point is that the quantity we are seeking—the redox asymmetry, ΔE—is usually obtained by electrochemistry for weakly interacting, asymmetrically coordinated sites (e.g. $\Delta E \sim E_{1/2}(6+/5+) - E_{1/2}(5+/4+)$). In the current experiment, however, ΔE is purely a nonequilibrium quantity and is therefore undetected in the equilibrium electrochemical measurements. (In terms of the existing theory of optical electron transfer,[23a] defining the mixed-solvent effect as a nonequilibrium contribution to ΔE (eq 6) is somewhat unusual. Nevertheless, the definition is appropriate if, for example, selective solvent binding at the ammine ligand sites is viewed as secondary coordination. The overall process is then akin to electron transfer to be followed by "ligand substitution" in the second sphere.[33] The time scale of the electrochemical experiment is such that only the energetics of the overall process are measured, yielding $\Delta E = 0$ for a symmetrical reaction. On the other hand, eq 6 yields a value of ΔE appropriate to the electron-transfer step in isolation, which for $x \neq y$ is not symmetrical.)

In Figure 4, the value of ΔE obtained from eq 6 has been plotted vs. the solvent mole fraction. The result is remarkable; it predicts via eq 4 that a sharp maximum in E^{MMCT} will appear at $m_{Me_2SO} = 0.03$. Comparison to Figure 2 confirms the prediction and shows

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[32] See, for example: (a) Timmermans, J. *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*; Interscience: New York, 1959. (b) Janz, G. J.; Tomkins, R. P. T. *Nonaqueous Electrolytes Handbook*; Academic: New York, 1972; Vol. 1.

[33] Besides accounting for the mixed-solvent results, such an approach begins to suggest how one might treat optical electron transfer in dimers displaying oxidation-state dependent primary ligation—for example, $(bpy)_2(H_2O)Ru^{II}(pz)Ru^{III}(OH)(bpy)_2^{4+}$. Indeed, this topic is a target for future investigations.

that ΔE accounts virtually quantitatively (after allowing for slight variations in χ_s) for the solvent compositional dependence of the optical electron transfer energy.

Before proceeding further, a significant limitation to eq 6 should be noted. In estimating ΔE from MLCT and LMCT transitions we have neglected to correct for solvent compositional effects upon L, L^-, and L^+ energies of solvation, although such energies (or at least their differences) clearly must contribute to the measured values of E^{LMCT} and E^{MLCT}. For the present system these contributions are small, especially in comparison to those occurring at the $(NH_3)_5Ru$ sites, and the use of eq 6 is justified. Nevertheless, for other systems eq 6 may be less applicable.

The observation of major energetic effects in optical electron transfer reactions has implications for related thermal electron exchanges. Unsymmetrical secondary coordination introduces an energy contribution in E^{MMCT} through ΔE in eq 4. As illustrated by Figure 5 the classical activation barrier (ΔG^*) for the corresponding thermal electron transfer should increase by $\sim 0.5\Delta E$. For $\Delta E = 1300$ cm^{-1}, $\Delta\Delta G^*$ is 1.9 kcal mol^{-1} and the expected influence upon the exchange rate constant is a decrease of about $1^1/_2$ orders of magnitude. We plan to search for such effects in pseudo-self-exchanges like $[(NH_3)_5Ru(\text{nicotinamide})]^{3+}/[(NH_3)_5Ru(\text{isonicotinamide})]^{2+}$. We are also attempting to extend the analysis to reactions that involve a change in *primary* coordination number, like the $Eu_{aq}{}^{3+/2+}$ self-exchange.

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Redox-State-Dependent Preferential Solvation of Ruthenium(II) and Ruthenium(III) Ammine Complexes. Implications for Electron-Transfer Processes in Mixed Solvents

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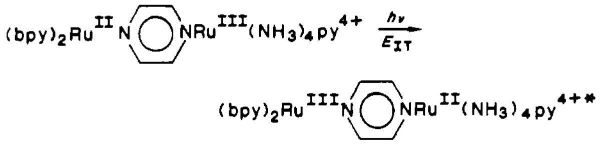
Preferential solvation of the asymmetric binuclear complex $(bpy)_2Ru^{II}Cl(pyz)Ru^{II/III}(NH_3)_4py^{3+/4+}$ by Me_2SO in acetonitrile has been studied via UV–vis, near-IR, and electrochemical techniques. It is found that the strong donor Me_2SO preferentially solvates the mixed-valence 4+ form of the dimer to a greater degree than the fully reduced 3+ form due to the relatively higher Lewis acidity of the ammine protons when coordinated to Ru(III). As one index of this, the equisolvation point of the II,II dimer is found at $\chi_{Me_2SO} = 0.104$ whereas that for the II,III form is at $\chi_{Me_2SO} = 0.003$. The degree of solvent "re-sorting" that must occur upon a change in redox state at the ruthenium ammine moiety as a function of χ_{Me_2SO} is quantified and found to go through a maximum at $\chi_{Me_2SO} \cong 0.019$. It is concluded that a solvent trapping barrier arising from nonequilibrium preferential solvation must be considered in situations involving electron-transfer processes of preferentially solvated solutes.

The importance of specific solvent–solute interactions in determining the redox thermodynamics and electron-transfer kinetics of transition-metal complexes has received considerable recent attention.[1-4] Investigations in this laboratory have shown that specific interactions of a hydrogen-bonding nature can be predominant in defining the solvent-dependent portion of the Franck–Condon barrier to optical electron transfer in asymmetric mixed-valence dimers such as (1).[5] (bpy = 2,2′-bipyridine, py



(1)

= pyridine, and E_{IT} denotes the energy of the intervalence-transfer absorption band maximum.) In this case it was found that strong Lewis base solvents (as indicated by large Gutmann donor numbers[6]) interacted with the solute in such a way as to both increase the redox asymmetry in the molecule by stabilizing the ruthenium(III)–ammine form of the dimer relative to the ruthenium(II)–ammine form and also increase the Franck–Condon energy of the transition by essentially adding a new dimension to the multidimensional potential energy surfaces defining it.

In mixed-valence systems where specific interactions with the medium are negligible, it has been amply demonstrated that the solvent-dependent portion of the Franck–Condon energy can be accounted for by using the dielectric continuum theory of nonequilibrium solvent polarization developed by Marcus and Hush.[7-9] This form of solvent-imposed barrier arises from the fact that it is only the very high (optical) frequency portion of the mediums' polarizability that can remain in equilibrium with the rapidly changing charge distribution attending electron-transfer events. On the basis of the geometric approximation for the donor–acceptor pair of two spheres with radii small compared to their center–center distance, the solvent barrier can be expressed as[7-9]

$$\lambda_{\mathrm{outer}} = e_0{}^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right)\left(\frac{1}{n^2} - \frac{1}{D_s}\right) \qquad (2)$$

where e_0 is the electron's charge, a_1 and a_2 are the radii of the sites, n^2 is the optical dielectric constant (square of the refractive index), and D_s is the static dielectric constant.

In this paper we wish to report on investigations carried out on the molecule shown in (1) in solvent mixtures of the moderate-donor-strength solvent acetonitrile (donor number = 14.1) and the high-donor-strength solvent dimethyl sulfoxide, Me_2SO (donor

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