Probing the Molecular Basis of Solvent Reorganization in Electron-Transfer Reactions

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Optical electron transfer in the mixed-valence dimer $[(NH_3)_5Ru^{II}\text{-}4,4'\text{-bpy-}Ru^{III}(NH_3)_5]^{5+}$ has been investigated in mixed solvents (acetonitrile + dimethyl sulfoxide) in order to probe molecular aspects of solvent reorganization. The basis for extracting information at the molecular level lies in the phenomenon of selective solvation and the resulting ability to vary the composition of the dimer's primary solvation layer largely independently of the predominant bulk solvent composition. This enables one to probe the first molecular layer of solvent separately from the rest. From the optical electron-transfer data, corrected for unsymmetrical selective solvation effects, we find that nearly all of the solvent reorganizational energy originates from reorientations occurring within the first molecular solvent layer. The reorganization energy *per solvent molecule* is fairly large in the first layer (ca. 125–150 cm^{-1}), indicating extreme librational (or other) excitation. Somewhat surprisingly, the molecular picture which emerges from our work is broadly consistent with the predictions of a simple solvent dielectric continuum theory.

Introduction

Solvent reorganization is a key feature of electron-transfer processes in polar media.[1] The electrostatic response of solvent dipoles to a change in electronic charge distribution creates a basis for valence trapping, as shown schematically in Figure 1. From existing theories of electron transfer the magnitude of the trapping or "reorganization" energy, χ_s, is given by[1,2]

$$\chi_s = e^2(1/r - 1/d)(1/D_{op} - 1/D_s) \qquad (1)$$

where e is the unit electronic charge, r is the radius of the trapping site, d is the distance between sites, and D_{op} and D_s are the solvent's optical and static dielectric constants, respectively. For corresponding thermal self-exchanges in homogeneous solution, the solvent-based activation energy, ΔG_s^*, equals $\chi_s/4$.[1,2]

Although eq 1 has been quite successful in describing solvent effects in electron transfer,[3,4] its use has been in a certain sense frustrating because it obscures molecular details. The equation is based on a model of the solvent as a dielectric continuum, rather than a molecular substance, and the pertinent input parameters are characteristic of the bulk solvent. In contrast, our desire has been to understand the *molecular* basis of solvent reorganization. Among the questions we want to answer are the following: (1) Which solvent molecules, and how many, are involved in solvent reorganization? (2) What are the magnitude and nature of the reorganization energetics at the molecular level?

We have been able to address both questions experimentally using the archetypical system $[(NH_3)_5Ru^{II}\text{-}4,4'\text{-bpy-}Ru^{III}(NH_3)_5]^{5+}$ (4,4'-bpy is 4,4'-bipyridine). Our strategy is based on the phenomenon of selective solvation. In mixtures of acetonitrile and dimethyl sulfoxide (DMSO) it is possible to achieve a situation approaching that sketched in Figure 2, i.e., nearly complete secondary coordination by DMSO but with bulk solvation chiefly by CH_3CN.[5] This effect enables one to probe the first molecular layer of solvent independently from the rest.

The probe we have chosen is the transition energy (E_{op}) for optical electron transfer:[4]

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

From Hush's theory,[2] E_{op} and χ_s are interrelated by

$$E_{op} = \chi_s + \chi_i + \Delta E + \Delta E' \qquad (3)$$

where χ_i is the inner shell or bond reorganization energy, ΔE is the difference in free energy[6] between vibrationally and electronically relaxed initial and final states, and $\Delta E'$ corresponds to any additional electronic contributions from spin–orbit coupling and ligand-field asymmetry.[7-9] We have shown elsewhere that χ_i and $\Delta E'$ are evidently independent of solvent composition and together equal to ~4800 cm^{-1}.[8] The quantity ΔE is zero in pure solvents but can attain a finite value in mixed solvents due to unsymmetrical selective solvation. Fortunately, ΔE can be independently and quantitatively assessed from metal-to-ligand (MLCT) and ligand-to-metal charge-transfer (LMCT) transitions.[5]

In this article we employ eq 3 and appropriate experimental data to extract χ_s from E_{op}. The way in which the solvent reorganization energy depends on both the bulk solvent composition and the composition of the first solvation layer is examined, and the significance and implications of the results are discussed.

Experimental Section

Materials. $[(NH_3)_5Ru(dmapy)](PF_6)_2$ (dmapy is (dimethylamino)pyridine) was prepared by a literature method.[10] In some preparations, workup of the Ru^{II} form led spontaneously to the Ru^{III} compound, apparently by air oxidation. Otherwise, the Ru^{III} form was obtained in situ from $(NH_3)_5Ru^{II}(dampy)^{2+}$ by oxidation with Br_2 vapor. $[Ru(bpy)_3](PF_6)_2$ (bpy is 2,2'-bipyridine) was obtained from an aqueous solution $[Ru(bpy)_3](Cl)_2$ (Aldrich) by precipitation with NH_4PF_6. $[(NH_3)_5Ru\text{-}4,4'\text{-bpy-}Ru(NH_3)_5](PF_6)_4$ was synthesized by combining $[(NH_3)_5Ru(OH_2)](PF_6)_2\cdot 2H_2O$ and 4,4'-bpy in 2:1 stoichiometry in deaerated acetone and allowing the mixture to react in the dark under argon for ~2 h.[11,12] The resulting red solution was added to a tenfold volume excess of stirring ether. The crude dimer (red powder) was isolated on a glass frit by vacuum filtration. In our hands, this method yielded samples containing significant amounts of $[(NH_3)_5Ru(4,4'\text{-bpy})](PF_6)_2$. The presence of the monomer is easily detected by comparing the visible region absorption spectrum in unbuffered water with that in 0.1 M HCl. In acid, protonation of the remote nitrogen of the bridging ligand shifts the monomer absorption maximum to lower energy, whereas the dimer is unaffected. A straightforward, but relatively low yield (40–60%) method of purifying the dimer was devised. First the crude product was dissolved in a small amount of acetonitrile, to which a similar amount of toluene was added. Rotary evaporation of the aceto-

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[1] Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

[2] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391.

[3] See, for example: Sullivan, B. P.; Curtis, J. C.; Kober, E. M.; Meyer, T. J. *Nouv. J. Chim.* **1980**, *4*, 683.

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[11] Tom, G. M.; Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 7827.

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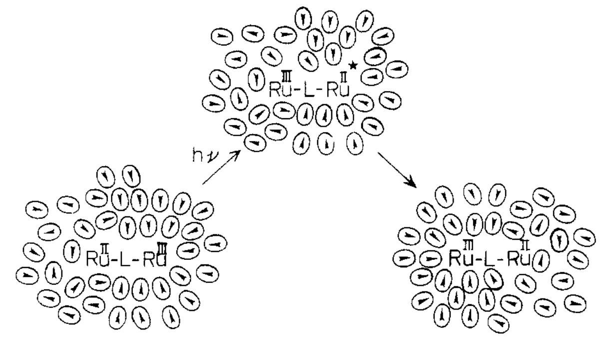


Figure 1. Schematic representation of the response of dipoles to a charge in electronic charge distribution upon optical electron transfer.

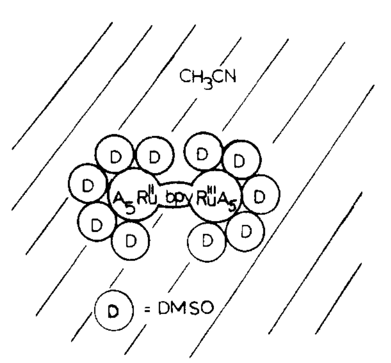


Figure 2. Schematic representation of selective solvation of $[(NH_3)_5Ru\text{–}4,4'\text{-bpy–}Ru(NH_3)_5]^{5+}$ by DMSO in acetonitrile-rich solution.

nitrile led to preferential precipitation of the dimer which was isolated by filtration. A second crop of partially purified dimer could be isolated by repeating the procedure with the filtrate. Remaining monomeric impurities were removed by stirring the dried precipitate for several minutes in the dark in each of 3 or 4 aliquots of warm CH_2Cl_2. The 5+ dimer was obtained in situ from the purified 4+ ion with Br_2 vapor as the oxidant. The electrochemical and UV–vis–near-IR spectral properties of the 4+ and 5+ dimers agreed with literature reports.[11] Prepurified solvents were obtained from commercial sources (Burdick and Jackson, Aldrich, Fischer). The majority of the near-IR spectra were obtained in CD_3CN and $(CD_3)_2SO$ (Aldrich) because of the wider spectral windows available and, more importantly, because of improved signal-to-noise ratios.

Measurements. Absorption spectra were measured with Perkin-Elmer 330 and 320 spectrophotometers. Band maxima could be reproducibly determined to whithin ±7 nm in the near-IR region (±10 to 12 nm for DMSO mole fraction of <0.05) and ±0.3 nm in the visible region, provided that the instrument calibration was checked periodically against the 656.1-nm deuterium source line. (For the ammine complexes, measurements in the visible region to within 1 nm were deemed sufficient.) To obtain accurate NIR data, we found it necessary to avoid the use of molecular sieves as solvent drying agents, because of artifacts from small particle light scattering, and similarly to employ dilute dimer solutions (ca. 0.2 mM), especially in acetonitrile-rich solvents.

Refractive index (n) measurements were made with an Abbé refractometer and a polychromatic source, after calibration with nine reference solvents. The measurement precision was ±0.001.

Results

Absorption maxima for metal-to-ligand charge transfer (E^{MLCT}) in $(NH_3)_5Ru^{II}\text{–}4,4'\text{-bpy–}Ru^{III}(NH_3)_5{}^{5+}$ and ligand-to-metal charge transfer (E^{LMCT}) in $(NH_3)_5Ru^{III}(dmapy)^{3+}$ were determined in 0.1 (or smaller) mole fraction (m) increments in acetonitrile/DMSO mixtures and are listed in Table I. Similar data were obtained for MLCT in $Ru(bpy)_3{}^{2+}$, as shown in Figure 3. Also contained in Figure 3 is a plot of $1/D_{op}$ ($= 1/n^2$) vs mole fraction of DMSO. Values for n are listed in Table I. In Figure 4, we show how the energy for metal-to-metal charge transfer (E_{op}) in eq 2 varies with solvent composition in acetonitrile/DMSO mixtures.

TABLE I: Solvent Dependence of Charge-Transfer Spectral Data in Mixtures of Acetonitrile and DMSO

m_{DMSO}	E^{MLCT}, $cm^{-1} \times 10^3$ [a]	E^{LMCT}, $cm^{-1} \times 10^3$ [b]	ΔE [c]	n [d]
0.000	19.01	16.92	0.08	1.347
0.010	18.80	17.98	0.93	1.350
0.020	18.55	18.38	1.08	1.351
0.030	18.48	18.48	1.11	1.352
0.035	18.38	18.54	1.07	1.353
0.050	18.25	18.66	1.06	1.356
0.100	17.92	18.87	0.94	1.367
0.150	17.67	18.94	0.76	1.376
0.200	17.48	18.98	0.61	1.383
0.300	17.30	19.01	0.45	1.399
0.400	17.18	19.01	0.34	1.413
0.500	17.09	19.01	0.25	1.428
0.600	17.01	19.01	0.17	1.440
0.700	16.96	19.01	0.12	1.455
0.800	16.92	19.01	0.08	1.463
0.900	16.88	19.01	0.04	1.476
1.000	16.84	19.01	0.00	1.483

[a] Absorption maximum for metal-to-ligand charge transfer in $(NH_3)_5Ru^{II}\text{–}4,4'\text{-bpy–}Ru^{III}(NH_3)_5{}^{5+}$. [b] Absorption maximum for ligand-to-metal charge transfer in $(NH_3)_5Ru^{III}(dmapy)^{3+}$. [c] Defined by eq 5. [d] Refractive index.

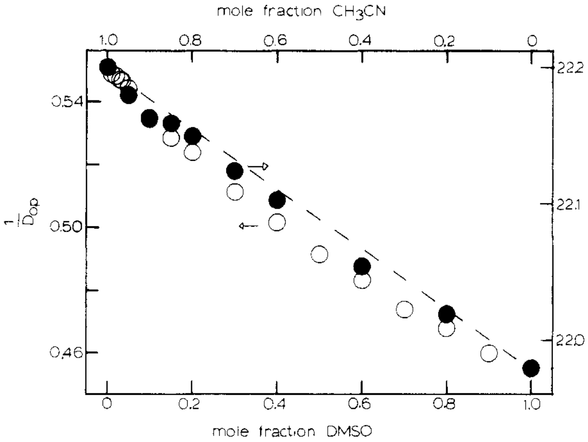


Figure 3. Dependence on mixed-solvent composition of (●) E^{MLCT} for $Ru(bpy)_3{}^{2+}$ and (○) $1/D_{op}$. Dashed line corresponds to a hypothetical linear relationship.

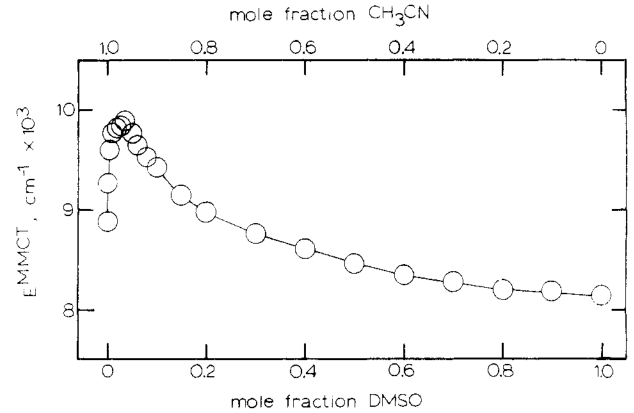


Figure 4. Dependence of E_{op} for MMCT in $[(NH_3)_5Ru^{II}\text{–}4,4'\text{-bpy–}Ru^{III}(NH_3)_5]^{5+}$ on solvent composition in acetonitrile/DMSO mixtures.

Discussion

Our results for charge-transfer transitions in $[(NH_3)_5Ru(dmapy)]^{3+}$ and $[(NH_3)_5Ru\text{–}4,4'\text{-bpy–}Ru(NH_3)_5]^{5+}$ are largely in accord with our earlier report,[5] while the results for $Ru(bpy)_3{}^{2+}$ in pure CH_3CN and pure DMSO agree well with those of Kober,

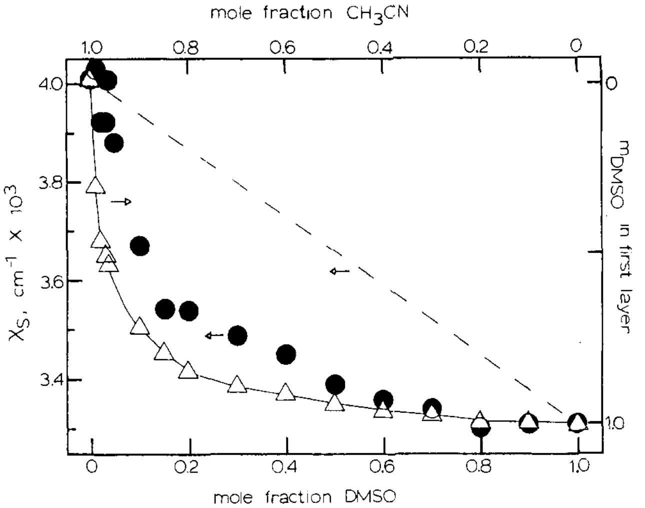
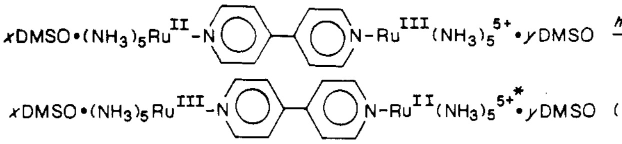


Figure 5. Dependence on bulk solvent composition of (●) χ_s for optical electron transfer in $[(NH_3)_5Ru^{II}\text{–}4,4'\text{-bpy–}Ru^{III}(NH_3)_5]^{5+}$ and (△) first solvation layer composition (see text). Dashed line corresponds to a hypothetical linear relationship between χ_s and bulk solvent composition.

Sullivan, and Meyer.[13] Where differences do exist (typically a few nanometers) we believe the present results to be more accurate based on repeatability, higher precision, and the care taken to eliminate artifacts.

Perhaps the most striking feature of the data is the sharp peak in the E_{op} vs m plot in Figure 4. We showed in an earlier report[5] that this effect arises from unsymmetrical selective solvation of the dimer by DMSO. Although both the $(NH_3)_5Ru^{II}$ and $(NH_3)_5Ru^{III}$ fragments are selectively solvated (see Table I), the effect is larger for the more highly charged fragment. As shown in eq 4, for $x \neq y$ optical excitation creates a high-energy redox



(4)

isomer; $(NH_3)_5Ru^{III}$ is trapped in a secondary coordination environment appropriate to $(NH_3)_5Ru^{II}$, and vice versa. From ref 5, the additional energetic cost, ΔE, for creating an unsymmetrically solvated excited state in the optical electron-transfer process can be calculated from energies for ligand-to-metal and metal-to-ligand charge transfer in pure and mixed solvents:

$$\Delta E = E^{MLCT}(\text{mixed}) + E^{LMCT}(\text{mixed}) - E^{MLCT}(\text{pure}) - E^{LMCT}(\text{pure}) \quad (5)$$

Table I lists the ΔE values thus obtained.[15]

To obtain values of χ_s, we resort to eq 3 together with the available values for E_{op}, $\chi_i + \Delta E'$, and ΔE. The resulting estimates are plotted vs m_{DMSO} in Figure 5. In the figure we have also included a plot of the compositon of the *first* solvation layer vs the bulk solvent composition. The estimates of the first-layer composition were obtained from E^{LMCT} and E^{MLCT} values by noting that the basis of solvatochromism in these transitions is in specific, short-range ligand–solvent hydrogen-bonding interactions,[10] which necessarily are confined to the first solvation sheath, and by assuming that the magnitudes of the solvatochromic shifts are linear in the local solvent composition.[16] Finally, included in Figure 5 is a dashed line corresponding to a hypothetical linear relationship between χ_s and bulk solvent composition.

An examination of Figure 5 suggests two possible limiting cases for the dependence of the reorganization energy upon the solvent composition. In case 1 the number of solvent molecules reorganized would be so large in comparison to the number contained in the hydrogen-bonded first layer that this initial layer would provide a negligible contribution to the overall reorganization energy. χ_s would then be expected to vary linearly with $1/D_{op}$ and almost linearly (vide infra) with the bulk solvent composition. In case 2, the number of molecules involved would be sufficiently small that *only* the first solvation layer would reorganize. Case 2 behavior would lead to a dependence of χ_s on the composition exclusively of the first solvation layer.

From Figure 5 the experimental results clearly correspond more closely to case 2 than case 1 behavior. For example, at $m_{DMSO} = 0.2$ bulk solvation is chiefly by acetonitrile and yet χ_s has a value similar to that in pure DMSO. In fact, a model consistent with the observed experimental behavior would be one in which roughly 75% of the reorganization energy originates in the first layer.

Before proceeding further, however, alternative explanations should be considered. One possibility is that the deviation of χ_s from bulk mole fraction statistics is simply due to a nonlinear dependence of the dielectric parameter, $1/D_{op} - 1/D_s$, on solvent composition. Figure 3 shows that there is indeed a slight nonlinearity in $1/D_{op}$ vs m, but the curvature is insufficient to account for the χ_s data. (A consideration of the differences and relative magnitudes of D_{op} and D_s reveals that, for the acetonitrile–DMSO pair, changes in $1/D_s$ can be neglected.) A less direct but possibly more relevant measure of $1/D_{op}$ (i.e., one obtained in the immediate vicinity of a metal complex) is available from appropriate metal-to-ligand charge-transfer transitions. Thus, Kober et al. have shown that values of E^{MLCT} for $M(bpy)_3^{2+}$ complexes (M = Ru, Os) in a series of pure solvents can be fit with good linearity to $1/D_{op}$ or to the more complicated function $(1 - D_{op})/(2D_{op} + 1)$.[13] Furthermore, Marcus has outlined a theoretical basis for the correlation.[17] Figure 3 shows our results for MLCT in $Ru(bpy)_3^{2+}$ in mixtures of acetonitrile and DMSO. Consistent with the direct measurements, the MLCT experiment shows an approximate linearity for $1/D_{op}$ vs m and, with the bulk n^2 measurements, eliminates the proposed alternative explanation.

A second explanation is one suggested in a related context by Brunschwig, Ehrenson, and Sutin. To account for the observed dependence of E_{op} on solvent in the decaammine dimer for a series of pure solvents, they hypothesized that the first solvent layer might be dielectrically saturated. This would lead to abnormally small local values for D_s ($\approx D_{op}$) and effectively increase the trapping site radius in eq 1 by an amount less than or equal to the thickness of the first solvent layer.[19] Such an hypothesis is certainly reasonable, especially in view of the relatively large ionic charges and the propensity of ammonia ligands to immobilize solvent molecules by hydrogen bonding. Rather than yielding the observed result, however, this model (in the limit of complete saturation) predicts an *independence* of χ_s on first-layer composition, at least for solvent molecules of comparable diameter. Dielectric saturation appears not to be a fully viable and complete explanation for our observations. Nevertheless, it should be noted that *partial* dielectric saturation (as proposed in ref 18) could play a role in optical electron-transfer reactions.

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(13) Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098.

(14) The assumptions contained in eq 5 have been described in ref 5. The most important one is that the $(bridge)^+$ or $(bridge)^-$ state created by charge transfer is not significantly preferentially solvated relative to the $(bridge)^0$ state. Also, it should be noted that because of spectral interferences, values for E^{LMCT} were obtained by using a monomeric surrogate, rather than the mixed-valance ion itself.[5] The reliability of this strategy is discussed in ref 5.

(15) In eq 5 and Table I, DMSO was designated as the "pure" solvent; acetonitrile could just as well have been used. The observation of a nonzero ΔE value for pure acetonitrile is unexpected. Its magnitude can be taken as a combined indicator of the limits to the validity of eq 5[14] and the uncertainties in the spectral measurements.

(16) See, for example: Langford, C. H.; Tong, J. P. K. *Pure Appl. Chem.* **1977**, *49*, 93.

(17) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 1261.

(18) Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657.

(19) To achieve a fit of the observed dependence of E_{op} on $(1/D_{op} - 1/D_s)$ (slope = 7800 cm^{-1}, ref 8) to eq 1, using r as an adjustable parameter and ignoring radial molecularity in the solvent, a thickness increment of 2.5 Å is required. If, in place of a two-sphere model (eq 1), an excluded-volume, ellipsoidal-cavity model is used to calculate χ_s (see, for example, ref 18), the required increment is ca. 1.5 Å.

A third alternative is that the χ_s values are dominated by contributions from the reorganization of the ligand–solvent hydrogen bonds themselves,[20] in place of nonspecific charge/dipole interactions of the kind envisioned in Marcus–Hush theory.[1,2] Possible evidence for such behavior exists for a related dimer, $(NH_3)_5Ru^{III}(pyrazine)–Ru^{II}(bpy)_2Cl^{4+}$,[20c] and indeed such an explanation is consistent with our observation of a close correspondence between χ_s and first-layer composition. Nevertheless, two points argue against it. First, limiting χ_s values in a series of pure solvents clearly vary with $1/D_{op} - 1/D_s$ rather than with solvent hydrogen-bonding (HB) parameters,[7,8] although a weak secondary correlation to HB parameters may exist.[8] Secondly, addition of DMSO to acetonitrile-rich solutions in the mixed-solvent experiment should lead to an initial *increase* in χ_s, since substitution of CD_3CN by DMSO in the secondary coordination sphere increases the strength of ligand–solvent HB interactions. Instead, a systematic decrease occurs (Figure 5).

Given that the experiment indeed does appear to indicate that roughly 75% of the classical solvent reorganization energy originates in the first layer, the implications are significant. First, solvent reorganization is evidently a relatively short range phenomenon. The first layer thickness in either DMSO or acetonitrile is ca. 4 Å based on bond lengths and van der Waals radii. This suggests that encapsulation or isolation of small-radius trapping sites (perhaps by micelles?) could have a profound effect on their redox reactivity simply by eliminating short-range solvent contributions to activation energies. Similarly, our results imply that in naturally occurring "encapsulated" or embedded systems, like metalloproteins, the dielectric medium of interest will be the immediate protein environment.[21] External solvent, if more than a few angstroms distant, would not be expected to contribute measurably to valence trapping.

There may also be consequences in polymeric systems. In the emerging area of redox conductivity,[22] the microscopic conduction mechanisms in polymeric materials is not yet well-understood. What is known is that redox conductivity can be modeled as site-to-site electron hopping.[22] Our observation of predominantly short-range solvent reorganization suggests that, even in a constrained polymeric environment, sufficient solvent may exist simply from swelling to create significant reorganizational demands and to contribute to the hopping barrier. (An intriguing observation is that in at least some instances conductivity in redox polymers increases upon removal of solvent.[23])

One additional observation concerns electron-transfer dynamics. For adiabatic reactions in solution there is increasing evidence that solvent relaxation processes can define the dynamics.[24] In polar solvents, however, a range of relaxation times exists. What is often chosen theoretically is the longitudinal relaxation time. Implicit in this choice is a lack of distinction between "near" and "far" solvent molecules, i.e., a solvent continuum.[25] Recently, Wolynes has pointed out that if a molecular description is adopted (the "mean spherical approximation"), a somewhat longer time (typically, a factor of 5) is expected for relaxation of molecules closest to the redox trapping site.[25] ("Closest" in the Wolynes MSA treatment corresponds to the first few layers, rather than the first layer only.) Our observation that it is these closest molecules that largely define χ_s and therefore (presumably) ΔG_s^* is significant because it provides a logical basis for directing the dynamical analysis toward the initial solvent layers.

Finally, before leaving the topic of the distance dependence of χ_s, it is worth considering the predictions of the continuum model. One way to do this is to use eq 1 with progressively larger values of the trapping site radius. This approach has some precedence from the work of Abraham[26] and others[27] on the thermodynamics of ionic solvation. By using $r = 3.5$ Å and $d = 11.3$ Å in eq 1, one obtains a theoretical value of χ_s integrated over all distances. If r is now increased by one molecular increment (ca. 4.2 Å for DMSO), one can obtain a second χ_s value corresponding to reorganization beyond the first solvent layer. The difference between the two would be χ_s for the first layer only. Finally, the ratio of χ_s (3.5 Å) − χ_s (7.7 Å) to χ_s (3.5 Å) should define (approximately[28]) the fraction of the solvent reorganization energy originating in the first molecular solvent layer. The value obtained, ca. 0.8, is in surprisingly good agreement with the experimental estimate of ca. 0.75 inferred from Figure 5. Apparently, the continuum model can withstand dissection at the molecular level.

Let us examine a second major implication of the experimental results. From the observation that almost all of the reorganization occurs in the first solvent layer, we can conclude that the total number of solvent molecules contributing importantly to χ_s is relatively small. From the work of Reynolds et al. up to 10 DMSO molecules can bind preferentially to $Cr((NH_3)_5DMSO^{3+}$ in DMSO/water mixtures.[29] Assuming a similar limiting value (j) for each of the pentaamine–Ru fragments in acetonitrile/DMSO mixtures, the first-layer reorganizational energy *per molecule* can be calculated. Based on χ_s (first layer) $\approx 0.75\chi_s$ (total) and $j = 20$, the quantity is 125–150 cm^{-1} per solvent molecule. This value is surprisingly large. For comparison, the inner-shell reorganization energy per ligand, based on a Ru–N bond length change of 0.04 Å for NH_3,[30] is only about 90 cm^{-1}. According to Ulstrup[31] the reorganized solvent modes are, apparently, low-frequency (1–10-cm^{-1}) collective motions—perhaps librations. If Ulstrup's picture is correct, our results imply extreme excitation, i.e., $S = E/h\nu = 12–150$ per solvent mode in the decaammine dimer system. If the modes are significantly anharmonic, the value of S could be larger.

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Registry No. DMSO, 67-68-5; $[(NH_3)_5Ru^{II}\text{-}4,4'\text{-bpy-}Ru^{III}(NH_3)_5]^{5+}$, 54065-65-5; $[(NH_3)_5Ru(dmapy)](PF_6)_2$, 83477-22-9; $[(NH_3)_5Ru(4,4'\text{-bpy})](PF_6)_2$, 94070-17-4; acetonitrile, 75-05-8.

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(28) The analysis is approximate because the limit of strict applicability of eq 1 is $2r \leq d$. Presumably other continuum models could be employed (cf. ref 18) if a more exact analysis were desired.

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