

Does Marcus–Hush Theory Really Work? The Solvent Dependence of Intervalence Charge-Transfer Energetics in $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{--}4,4'\text{-bipyridine--Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$ in the Limit of Infinite Dilution

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Because of concern about ion-pairing artifacts, the solvent dependence of the intervalence charge-transfer absorption energy for a prototypical mixed-valence system, $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{--}4,4'\text{-bipyridine--Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$, has been reexamined in the limit of infinite dilution. New data are reported for 14 solvents. While one of these (hexamethylphosphoramide) yields anomalous energetics, the absorption energies for the remaining 13 solvents agree qualitatively with the predictions of the Marcus–Hush theory (i.e., two-sphere dielectric continuum theory). On a quantitative basis, however, there is substantial disagreement with theory, at least when the charge-transfer distance is equated with the metal-to-metal separation distance (as conventionally done). Replacement of this distance with a much shorter distance inferred from by electronic Stark-effect spectroscopy (Oh et al. *J. Am. Chem. Soc.* **1990**, *112*, 8161) leads to a 3-fold decrease in the magnitude of calculated solvent reorganizational contributions to the overall intervalence energy (and therefore, very good agreement with experiment). Unfortunately, the use of such a short charge-transfer distance ($d = 5.1 \pm 0.7 \text{ \AA}$) also leads to a violation of one of the boundary conditions for use of the two-sphere model. Reformulation of the problem in terms of a generalized dipole-inversion, dielectric cavity problem (Brunschwig et al. *J. Phys. Chem.* **1986**, *90*, 3657), however, leads to nearly perfect agreement between theory and experiment. Additional analysis shows that experiment now also agrees reasonably well with theory regarding the magnitude of solvent-independent energy contributions. Finally, it is noted that downward revision in the estimated charge-transfer distance (from 11.3 to 5.1 \AA) leads to a substantial upward revision in the experimental (i.e., oscillator-strength based) estimate of the electronic coupling element, H_{if} , for intervalence transfer. Further analysis, based on published data for longer bridges, suggests that charge-transfer distance revisions can also account (at least partially) for the seemingly weak dependence of H_{if} on distance in decaammineruthenium systems.

Introduction

Optical intervalence charge-transfer (IVCT) absorption measurements, especially for symmetrical mixed-valence species, have provided a convenient and powerful means for assessing directly the total reorganizational barrier to electron transfer.¹ For strongly valence-localized symmetrical systems the IVCT absorption maximum ($E_{\text{op}}^{\text{IVCT}}$) can be written approximately as²

$$E_{\text{op}}^{\text{IVCT}} = \chi_s + \chi_v + \Delta E' \quad (1)$$

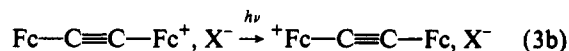
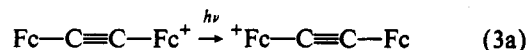
where χ_s is the solvent reorganization energy, χ_v is the internal or vibrational reorganization energy, and $\Delta E'$ accounts for any additional energy associated with excitation to either a spin-orbit or ligand-field excited state.^{3–5} Typically, χ_s and χ_v have been separated by performing absorption measurements in a range of solvents^{4–9} or by evaluating intervalence energetics as a function of bridge length or charge-transfer distance, d .^{10,11} (Note that χ_v is not expected to vary with d .) Simple Marcus–Hush theory predicts the following dependence of χ_s (and therefore, $E_{\text{op}}^{\text{IVCT}}$) on solvent and structural properties:^{1,12}

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

In eq 2, e is the fraction of charge actually transferred (unity for a fully localized system), D_{op} is the optical dielectric constant of the solvent, D_s is the static dielectric constant, and r is the molecular trapping site radius. It should be noted that eq 2 is derived from a nonequilibrium polarization model¹² which (a) treats the solvent as dielectric continuum and (b) views the ligand-bridged mixed-valence sites as simple conducting spheres.

A number of studies^{3–11} have demonstrated at least qualitative agreement between experiment and the predictions of eqs 1 and 2. Over the last few years, however, two general problems have

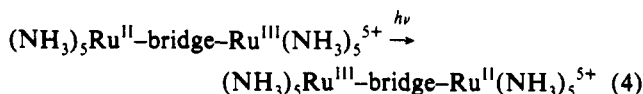
come to light. First, several groups, including our own, have shown (in contrast to the simplest expectations from eqs 1 and 2) that $E_{\text{op}}^{\text{IVCT}}$ is sensitive to both chromophore concentration and the presence of added electrolyte.^{13–15} We have further shown that the energy effects arise specifically from a symmetry reduction effect associated with ion pairing or with higher-order ionic aggregation.¹⁵ For example, for the ordinarily symmetrical IVCT transition in acetylene-bridged biferrocene monocation (eq 3a), counterion pairing (eq 3b) clearly renders the initial and final



charge-transfer states energetically (i.e., electrostatically) inequivalent. In some solvents, $E_{\text{op}}^{\text{IVCT}}$ for eq 3b and related equilibria can exceed that for eq 3a by as much as 2000 cm^{-1} .¹⁵ Depending on whether electron transfer in the corresponding thermal process is viewed as occurring sequentially or synchronously with ion translation, the extra energy associated with ion pairing can be viewed as either an unfavorable thermodynamic driving force (ΔE) or as an additional component of the total reorganization energy. In any case, Hendrickson and co-workers^{13b} have pointed out that these complications might well be more severe for more highly charged species—a contention at least partially supported by the studies of Lewis and co-workers of dithiaspirane-bridged decaammine complexes (5^+ total charge).¹⁴ One might question, therefore, the validity of earlier findings^{3,5} regarding IVCT solvent effects for highly charged systems.

The second general problem concerns the apparent lack of quantitative agreement with eq 2, despite qualitative behavior

consistent with the underlying theoretical description.^{5,9,11} This problem is perhaps most evident for valence-localized decaammine diruthenium systems (eq 4) for which (a) the dependence of



$E_{\text{op}}^{\text{IVCT}}$ on solvent dielectric properties (bridge = 4,4'-bipyridine) is apparently only about 40% as great as predicted by eq 2 (implying that χ_s is only ~40% as large as theoretically predicted),⁵ and (b) χ_v , obtained from the $\Delta E'$ -corrected intercept of a plot of $E_{\text{op}}^{\text{IVCT}}$ versus $1/D_{\text{op}} - 1/D_s$, is larger than predicted on the basis of independent crystallographic measurements.^{5,16} These quantitative discrepancies could conceivably be related to the ion-pairing effects noted above. Alternatively, they could be related to real deficiencies in the available continuum theory. We note, however, that a detailed consideration (by Brunschwig, Ehrenson, and Sutin)¹¹ of alternative continuum models (for example, dielectric cavity models)^{11,17-19} failed to improve agreement with experiment. A related suggestion that the disparities might originate with partial solvent dielectric saturation¹¹ seems to have been disproven (or at least discounted) by subsequent studies of IVCT in mixed solvents under conditions of selective solvation.²⁰

Given the possibility of ion-pairing artifacts and the apparently extensive disparities between experiment and theory, we felt that reevaluation of the solvent dependence of IVCT for the title complex under conditions of high dilution was important. We report new data for 14 solvents, obtained in the limit of infinite dilution. We find (a) only modest changes in IVCT energies in comparison to energies measured previously at finite ionic strength,^{3,5} but (b) reconciliation of the small measured χ_s values with theory, by inclusion in eq 2 of an alternative estimate²¹ of the IVCT distance (inferred from a recently obtained Stark-effect measurement²¹ of the maximum difference in ground-state/excited-state mixed-valence dipole (vector) size), (c) reconciliation of the apparently weak dependence of IVCT on bridge length,^{22,23} via similar considerations, and (d) reconciliation of χ_v from optical measurements, with χ_v from crystallographic studies,¹⁹ via a cavity analysis of the solvent component and via careful consideration of possible differences between measured absorption energy maxima and true "vertical" charge-transfer energies. We also find evidence for significantly greater initial-state/final-state electronic coupling than previously suspected.²⁴

Experimental Section

Solvents. Where possible, deuterated solvents were used for intervalence measurements because they provide an expanded region of transparency in the near-infrared region. Dimethyl-*d*₆ sulfoxide, acetonitrile-*d*₃, acetone-*d*₆, nitrobenzene-*d*₅, nitromethane-*d*₃, D₂O, and methanol-*d* were all purchased from Aldrich and used as received. Propylene carbonate (99+%, spectroscopic grade), *N,N*-dimethylformamide (99+%, spectroscopic grade), 1-methyl-2-pyrrolidinone (99%, spectroscopic grade), hexamethylphosphoramide (HMPA, 99%) and *N,N*-dimethylacetamide (99%) were purchased from Aldrich. Prior to use, most were passed through an activated alumina column (N₂ atmosphere) to remove residual water and/or colored impurities.

Syntheses. [(NH₃)₅Ru^{II}-4,4'-bpy-Ru^{III}(NH₃)₅](PF₆)₄ was prepared and purified as previously described.²⁰ The mixed-valent ion, (NH₃)₅Ru^{II}-4,4'-bpy-Ru^{III}(NH₃)₅⁵⁺, was obtained by four slightly different methods: (1) in situ by Br₂ vapor addition while monitoring the absorbance of the MMCT band, (2) in situ by using an equimolar amount of [Fe(2,2'-bipyridine)₃](PF₆)₃ as oxidant, (3) by first dissolving the 4⁺ ion in acetone, adding a stoichiometric amount of [Fe(2,2'-bipyridine)₃](PF₆)₃, evapo-

TABLE I: Solvent-Dependent Intervalence Absorption Energies and Dielectric Parameters

solvent	$E_{\text{op}}^{\text{IVCT}}$ (in diln), cm ⁻¹	$E_{\text{op}}^{\text{IVCT}}$ (ca. mM concn), ^a cm ⁻¹	$1/D_{\text{op}} - 1/D_s$
propylene carbonate	8350 ^b	8670	0.481
formamide	8650	8700	0.467
acetone- <i>d</i> ₆	8620		0.496
dimethylacetamide	8080	8540	0.459
dimethyl- <i>d</i> ₆ sulfoxide	8040	8150	0.438
dimethylformamide	8330	8590	0.462
acetonitrile- <i>d</i> ₃	8800	8800	0.526
1-methyl-2-pyrrolidinone	8120		0.432
hexamethylphosphoramide	7050 ^b		0.437
deuterium oxide	9550	9550	0.546
methanol- <i>d</i>	9120	9100	0.538
nitrobenzene- <i>d</i> ₅	7750	7750	0.388
benzonitrile- <i>d</i> ₅	7800	7850	0.388
nitromethane- <i>d</i> ₃	8250	8400	0.496

^a Data taken from refs 3 and 5. ^b Upper limit estimate; infinite dilution was not achieved for these solvents.

rating the acetone, and then finally dissolving the resulting 5⁺ ion in the solvent of choice, and (4) by first dissolving the 4⁺ ion in methanol, adding an excess of Br₂ vapor as oxidant, removing the solvent, redissolving the resulting 6⁺ species, adding a second equivalent of the 4⁺ species, evaporating the solvent again, and finally dissolving the resulting 5⁺ ion in the solvent of choice. Method 2 was preferred for most measurements; however, in HMPA as solvent, Fe(bpy)₃³⁺ and Br₂ were both spontaneously reduced. Thus method 3 was employed. In a few other instances tailing of the Fe(bpy)₃²⁺ visible region absorption into the near-infrared region caused spectral interferences. For those cases, method 1 was usually employed. We observed, however, that method 1 introduces water into the sample. This proved problematic in weakly basic solvents because of selective solvation of the ammine complex by H₂O; therefore, in these few instances method 4 was employed. It should be noted that under the high dilution conditions employed in our study we did not encounter the oxidant dependence in intervalence energies claimed by others.^{14b} We ascribe this to the successful avoidance of ion pairing effects.^{13,15}

Measurements. High dilution absorbance measurements were carried out with an OLIS-modified CARY 14 spectrophotometer by using long path length cells, essentially as previously described.^{4b} Infinite dilution was operationally defined as the point at which further dilution led to no further shift in the IVCT absorption maximum. This limit proved to be accessible experimentally for all solvents except HMPA and propylene carbonate. The reproducibility of the absorbance maximum was ±65 cm⁻¹ in most solvents, but ±100 cm⁻¹ in benzonitrile, nitrobenzene, 1-methyl-2-pyrrolidinone, and HMPA.

Results and Discussion

Solvent Dependence. Table I lists intervalence absorption energies for reaction 4 (4,4'-bpy as bridge) at infinite dilution in 14 solvents. Also listed are $E_{\text{op}}^{\text{IVCT}}$ values obtained previously at finite concentration (roughly millimolar in most cases). While some differences are evident (the infinite dilution values tend to be slightly lower) the agreement is generally quite close, indicating that solvent-dependent ion-pairing effects are not an overwhelming factor in the IVCT of the decaammine complex under typical experimental conditions. As this behavior contrasts with that for other mixed-valence ions,¹³⁻¹⁵ it is worth commenting on the origin of the differences. Three factors seem particularly important: (1) The target molecule, (NH₃)₅Ru-4,4'-bpy-Ru(NH₃)₅⁵⁺, is insoluble in the solvents most prone to ion-pairing artifacts (i.e., low dielectric solvents such as methylene chloride). (2) Because of stronger electronic coupling (higher IVCT extinction coefficient) the typical concentration for measurements with (NH₃)₅Ru-4,4'-bpy-Ru(NH₃)₅⁵⁺ is one to 1^{1/2} orders of magnitude less

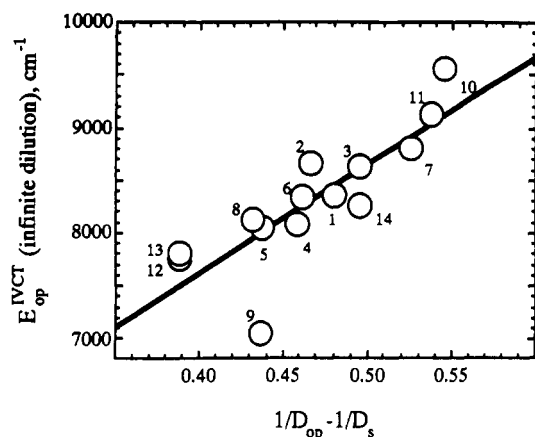


Figure 1. Intervalence absorption energy for $(\text{NH}_3)_5\text{Ru}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{III}}(\text{NH}_3)_5^{5+}$ (infinite dilution) vs $1/D_{\text{op}} - 1/D_s$. Numbering of solvents is given in Table I. Line drawn is the best-fit line to all data except that obtained in HMPA (point no. 9).

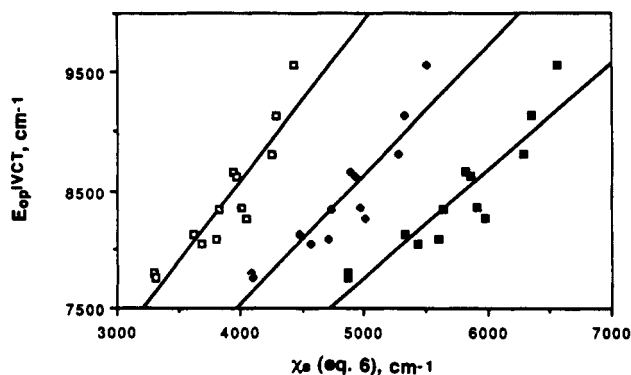
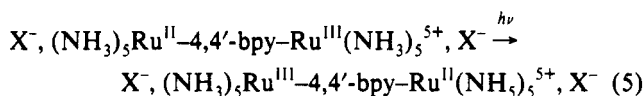


Figure 2. Experimentally measured $E_{\text{op}}^{\text{IVCT}}$ values (infinite dilution, Table I) vs calculated solvent reorganization energies (eq 6), based on $D_{\text{in}} = 2.0$, but with varying charge distances, d . Key to d values: (\square) 4.4 Å, (\blacklozenge) 5.1 Å, and (\blacksquare) 5.8 Å. Lines drawn are best-fit lines; see Table II.

than typically employed with dithiaspirane analogs¹⁴ (consequently, counter-ion pairing equilibria involving the former are driven much less toward completion). (3) The availability of two distinct charge centers in the mixed-valence chromophore could lead, under some conditions, to double ion-pairing (eq 5). In our



model, double ion pairing would have no energetic consequences for IVCT, because ion translation is no longer linked to electron transfer. While proof is lacking here, we have compelling experimental evidence for this "cancellation" effect for a related chromophore, $(\text{CN})_5\text{Fe}^{\text{II}}\text{-BPE-Fe}^{\text{III}}(\text{CN})_5^{5-}$ (BPE = bis(pyridyl)ethylene), in the presence of La^{3+} ions.²⁵

Returning to solvent effects, the infinite-dilution $E_{\text{op}}^{\text{IVCT}}$ values have been plotted in Figure 1 versus $(1/D_{\text{op}} - 1/D_s)$. Significant scatter is evident, but a correlation clearly does exist for all solvents except HMPA. The origin of the energy disparity for this solvent is unclear at present but appears not to be related to chromophore decomposition. For the remaining 13 solvents, a least-squares fit yields a slope (and standard error) of $9250 \pm 1300 \text{ cm}^{-1}$, an intercept (and standard error) of $4070 \pm 600 \text{ cm}^{-1}$, and for the individual values of $E_{\text{op}}^{\text{IVCT}}$, a standard deviation (σ) of 220 cm^{-1} . It is noteworthy that water, which we have previously suggested is anomalous,⁵ now yields an $E_{\text{op}}^{\text{IVCT}}$ value within 2σ of the best-fit line.

Comparisons to theory are possible via eqs 1 and 2. Based on a trapping site radius of 3.55 Å (appropriate for ruthenium

pentaammine), a charge-transfer distance of 11.3 Å (the metal-metal separation distance), and assuming transfer of unit electronic charge, eq 2 predicts a slope of $22\,500 \text{ cm}^{-1}$ for $E_{\text{op}}^{\text{IVCT}}$ vs $1/D_{\text{op}} - 1/D_s$. Importantly, the prediction exceeds by 2–3-fold the experimentally observed slope (Figure 1), implying that χ_s itself is greatly overestimated theoretically. As mentioned above, the "slope problem" has been observed previously and a variety of explanations has been suggested.^{5,11} Clearly, however, the discrepancy cannot be ascribed to ion pairing or aggregation effects.

A key insight and reasonable resolution of the theory/experiment discrepancy is provided by recent intervalence Stark-effect measurements.²¹ Oh and Boxer have observed that the maximum ground-state/excited-state dipole moment difference, $\Delta\mu$, for eq 4 is $28.5/fD$, where f is a local electric field correction.²¹ Furthermore, they note that $\Delta\mu$ for IVCT should equal ed . Taking f as 1.15 ± 0.15 (Boxer's estimate) and assuming, for the moment, transfer of unit electronic charge, a transition dipole length (or charge-transfer distance, d) of just $5.1 \pm 0.7 \text{ Å}$ is implied. This necessarily suggests significant changes in electron density in both pyridyl (py) rings during the nominal metal-to-metal charge-transfer process. The trapping sites are probably better modeled, therefore, as $\text{Ru}(\text{NH}_3)_5\text{py}^{n+}$ fragments. This, in turn, suggests a slightly larger effective trapping site radius: ca. 4.2 Å (where $r(\text{effective})$ has been taken as $(r_x r_y r_z)^{1/3}$). With these alternative estimates for d and r , eq 2 now predicts a slope of 4800 cm^{-1} for $E_{\text{op}}^{\text{IVCT}}$ vs $(1/D_{\text{op}} - 1/D_s)$, in fairly good agreement with Figure 1.²⁶ Unfortunately, however, with this choice of geometric parameters, a key boundary condition in the derivation of eq 2 (i.e., $d > 2r$)¹² is no longer satisfied. Quantitative application of the equation, therefore, is no longer justified.

An alternative theoretical approach, with more compatible boundary conditions, is the ellipsoidal cavity treatment.¹¹ Here, charge transfer is treated as a dipole inversion within a low dielectric cavity; the transition dipole length is given by the charge-transfer distance and the cavity size and shape ideally correspond to the size and shape of the mixed-valence ion. The analytical expression for χ_s obtained by Brunschwig et al. is¹¹

$$\chi_s = \frac{(\Delta e)^2}{R} \left[\left(\frac{1}{D_{\text{in}}} - \frac{1}{D_s} \right) \sum_{n=1}^{\infty} \frac{X_n}{I_n(D_{\text{in}}, D_s)} - \left(\frac{1}{D_{\text{in}}} - \frac{1}{D_{\text{op}}} \right) \sum_{n=1}^{\infty} \frac{X_n}{I_n(D_{\text{in}}, D_{\text{op}})} \right] \quad (6)$$

where

$$X_n = 2(2n+1)\{1 - (-1)^n\}P_n^2(\xi_k)Q_n(\lambda_0)/P_n(\lambda_0) \quad (7)$$

and

$$I_n(D_\alpha, D_\beta) = 1 - \frac{D_\alpha}{D_\beta} \left(\frac{\lambda_0 - P_{n+1}(\lambda_0)/P_n(\lambda_0)}{\lambda_0 - Q_{n+1}(\lambda_0)/Q_n(\lambda_0)} \right) \quad (8)$$

$$\lambda_0 = [(A^2/A^2 - B^2)]^{1/2} \quad (9)$$

In eqs 6–9, R is the interfocal length, D_{in} is the dielectric constant within the cavity, ξ_k equals d/R , P_n and Q_n are Legendre polynomials of the first and second kinds, A is the length of the semimajor axis, and B is the length of the two semiminor axes of the ellipsoid.

For the decaammine system, we have (somewhat arbitrarily) taken B and A to be 3.55 and 9.2 Å (or $3.55 + 11.3/2$), respectively. Following Brunschwig et al., D_{in} was assigned a value ranging from 1.8 to 2.2.¹¹ Finally, based on Boxer's work,²¹ d was given a value of $5.1 \pm 0.7 \text{ Å}$. To compare the theory with experiments, we have plotted $E_{\text{op}}(\text{expt})$ directly against χ (eq 6), for each of the 13 available solvents (Figure 2; HMPA excluded).

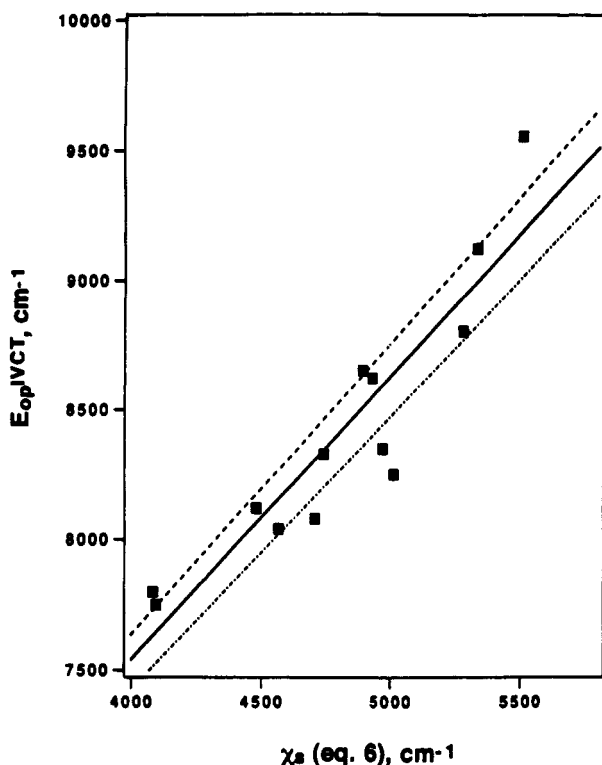


Figure 3. Experimentally measured E_{op}^{IVCT} values (infinite dilution, Table I) vs calculated solvent reorganization energies (eq 6), based on $d = 5.1$ Å, but with varying D_{in} . Data points and solid line are with $D_{in} = 2.0$. Dashed line is a best-fit line with $D_{in} = 1.8$. Dotted-dashed line is a best fit with $D_{in} = 2.2$. See also Table II.

TABLE II: Slopes and Fitting Parameters for Plots of Measured Intervalence Charge-Transfer Energies vs Calculated Solvent Reorganization Energies (Eq 6)^a

d , Å	D_{in}	slope ^b	correln ^b coeff r
4.4	2.0	1.36	0.916
5.1	2.0	1.09	0.917
5.4	2.0	1.00	0.916
5.8	2.0	0.91	0.914
5.1	1.8	1.05	0.909
5.1	2.2	1.12	0.913

^a Plots shown in Figures 2 and 3. ^b Based on 13 solvents (i.e., excluding HMPA).

The parameters of significance are the slope of the plot (ideally unity) and the overall correlation coefficient. (Evaluation on this basis permits us to avoid making assumptions regarding χ_v and $\Delta E'$ and to accommodate the fact that eq 6 (unlike eq 2) predicts a less than exact correlation between χ_s and $(1/D_{op} - 1/D_s)$.) From Figure 2 and Table II, slopes near unity (for $E_{op}(\text{expt})$ vs χ_s (eq 6)) are obtained in all cases. Furthermore, reasonable correlation coefficients are obtained (again excluding HMPA). Nevertheless, there are detectable variations in slope, and therefore χ_s , with model parameters. For example, increases in d lead (as expected) to increases in slope, while increases in D_{in} lead to decreases in slope. If D_{in} is set exactly equal to 2.0, then a slope of unity ($E_{op}(\text{expt})$ vs χ_s (eq 6); excluding HMPA) is obtained when d is 5.4 Å. Even without arbitrary manipulation of parameters, however, the dielectric cavity model clearly is able (with short charge-transfer distance²¹) to rationalize the experimentally observed solvent dependence.

Vibrational Reorganization. The availability of experimental data in a range of solvents, together with functional models for the expected solvent dependence, provide a basis for evaluating solvent-independent energy effects. For example, the energy intercept of the simple plot of E_{op} vs $1/D_{op} - 1/D_s$ (Figure 1) is expected to equal the sum of χ_v and $\Delta E'$. The latter has been estimated previously⁵ as ca. 1900 cm^{-1} , leaving ca. 2200 cm^{-1} as

the portion assignable to χ_v . Alternatively, in view of the discussion surrounding cavity models the sum of χ_v and $\Delta E'$ should equal the difference quantity, $E_{op}(\text{expt}) - \chi_s$ (eq 6). Using optimized parameters for χ_s ($D_{in} = 2.0$; $d = 5.4$ Å; slope = 1.00), the average difference quantity (13 solvents; HMPA excluded) is 3200 ± 420 cm^{-1} (2σ uncertainty). Again estimating $\Delta E'$ as ca. 1900 cm^{-1} , the value obtained for χ_v is 1300 ± 420 cm^{-1} .

For comparison, an analysis^{3,11} of crystallographically determined bond length differences¹⁶ between the d^5 and d^6 forms of the model complex, $\text{Ru}(\text{NH}_3)_5(\text{pyrazine})^{n+}$, has yielded a vibrational reorganization energy estimate of 1400 cm^{-1} , in fair agreement with the two-sphere analysis (Figure 1) and in almost exact (presumably fortuitously close) agreement with the cavity analysis. Nevertheless, there are at least a couple of reasons to be circumspect. First, the cavity analysis was somewhat arbitrarily optimized²⁶ (albeit, within the range of parameter uncertainties prescribed by the Oh and Boxer experiment). Second (and perhaps more importantly), we have recently been reminded^{27,28} that wavelength-dependent charge-transfer intensities scale not only with Franck-Condon overlaps (our primary assumption in interpreting the measured E_{op}^{IVCT}) but also with the inverse of the absolute absorption energy (a necessary consequence of the sum rule²⁹). For high-energy electronic transitions, the E^{-1} effect (for a given transition) is negligible. For low-energy transitions (such as symmetrical IVCT transitions), however, the effect can be significant, especially when absorption bands are broad. For example, correction of the IVCT absorption spectrum of the decaammine complex in nitromethane as solvent (by scaling the measured intensities by E^{-1}) leads to a 550- cm^{-1} red shift in the absorption maximum. This energy, rather than the simple absorption maximum, is the quantity most correctly identified with the upper-surface/lower-surface, vertical energy separation, and is therefore the quantity most appropriately utilized in eq 1. With this correction, we revise downward (by 550 cm^{-1}) our optical estimate of χ_v and now find less exact agreement with the crystallographic estimate.

Electronic Coupling Effects. Downward revision in the estimated charge-transfer distance suggests a reevaluation of electronic interactions as well. These are commonly evaluated via oscillator strength (spectral absorption) measurements. One limiting expression for the numerical relationship between absorption properties and the initial-state/final-state interaction energy (H_{if}) is²

$$|H_{if}| = 2.06 \times 10^{-2} (\epsilon_{\max} \Delta \bar{\nu}_{1/2} E_{op}^{IVCT})^{1/2} / ed \quad (10)$$

where ϵ_{\max} is the extinction coefficient at E_{op}^{IVCT} , $\Delta \bar{\nu}_{1/2}$ is the half-width of the absorption band and the other parameters have been defined previously. For the title complex, Sutton, Sutton, and Taube have reported a comproportionation-corrected H_{if} value of 460 cm^{-1} in water (based on $d = 11.3$ Å in eq 10).²⁴ If the d value inferred from Stark-effect measurements (i.e., 5.1 ± 0.7 Å) is used instead, the integrated IVCT spectrum yields $H_{if} = 1020 \pm 130$ cm^{-1} .³⁰ For electron transfer in the nonadiabatic limit (admittedly a limit not reached here), the kinetics are expected to scale as H_{if}^2 . Notably, revision in the estimate for d gives a 5-fold increase in H_{if}^2 . Even with the increase, however, the decaammine dimer must still be characterized as almost completely valence localized. From first-order perturbation theory,² the extent of delocalization, α^2 , is simply $(H_{if}/E_{op}^{IVCT})^2$. Taking E_{op}^{IVCT} as ca. 8000 cm^{-1} , we obtain $\alpha^2 = 0.016$.³¹

Finally, extension of the adjusted electronic analysis to lengthier polyene-bridged systems of the type $(\text{NH}_3)_5\text{Ru}^{II}\text{py}-(\text{CH}=\text{CH})_n-\text{pyRu}^{III}(\text{NH}_3)_5^{5+}$, where $n = 0-4$ ^{22,24,32} may account for the (apparently) remarkably small decrease in H_{if} with increasing donor-acceptor separation distance.^{22,23} For example, in quantitatively evaluating the available experimental data (IVCT

absorption spectra), Sutin has pointed out that H_{if}^2 drops by only a factor of 4 (or 6, based on the H_{if} values cited here) in extending the bridge from $n = 0$ to $n = 4$ (i.e., an overall molecular length change of ca. 9.4 Å).²³ This may be contrasted, for example, with a ca. 80-fold decrease in H_{if}^2 for the same distance change in the isopropylene-bridged osmium ammine/ruthenium ammine systems developed by Isied et al.³³ In Sutin's analysis of the polyene-bridged systems,²³ d was taken, logically enough, as the metal-metal separation distance (i.e., 11.3–20.7 Å). As noted above, Boxer's results²¹ suggest that $d = 5.1$ Å when $n = 0$. This leads (eq 10) to an approximately 5-fold increase in the estimate for H_{if}^2 . If an identical revision (presumably a reasonable upper limit) is made in the case where $n = 4$, d decreases from 20.7 to 14.5 Å, and H_{if} (via eq 10) increases from ca. 180 to 260 cm⁻¹. More importantly, the quantity of $H_{if}^2(n=0)/H_{if}^2(n=4)$ increases to ca. 15, bringing the optical measurements into closer agreement with the kinetics-based measurements³⁴ for the related isopropylene systems. Obviously, if the appropriate distance adjustment is less when $n = 4$, then the ratio could be even higher (ca. 30 if no adjustment is required).

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