

Energy Relationships in Optical and Thermal Electron Transfer. Temperature Dependence of an Intervalence Transfer Absorption Band

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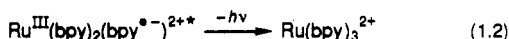
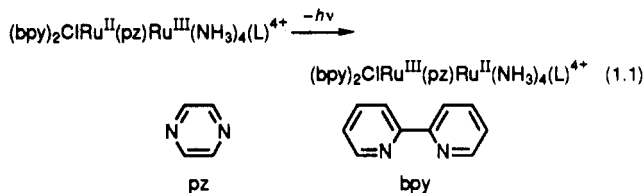
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The temperature dependence of the intervalence transfer (IT) band for the transition $[(\text{bpy})_2\text{ClRu}^{\text{II}}(\text{pz})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4+} \rightarrow [(\text{bpy})_2\text{ClRu}^{\text{III}}(\text{pz})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$ (pz = pyrazine; bpy = 2,2'-bipyridine) has been studied in CH_3OD and in a nitrile solvent mixture. The temperature dependences of $E_{1/2}$ for the component $\text{Ru}^{\text{III/II}}$ couples in this complex were also studied by cyclic voltammetry. The temperature dependence of the absorption band, which was quite large, $(\partial E_{\text{op}}/\partial T) = -10 \text{ cm}^{-1} \text{ K}^{-1}$ in CH_3OD , $\mu = 0.035 \text{ M}$, was found to be the same, within experimental error, as the temperature dependence of the difference between the $E_{1/2}$ values for the $\text{Ru}^{\text{III/II}}$ couples. This agreement provides experimental evidence that the absorption band energy includes the free energy change between the initial and final states and not just the change in enthalpy or internal energy. This is consistent with a model proposed by Marcus and Sutin for electron-transfer based on free energy surfaces despite the inability of the dielectric continuum model to account for the solvent-dependent behavior of this dimer. A quantum mechanical model is also found to predict that the absorption band energy should be temperature dependent because the band energy depends upon the free energy change. This model is based on potential energy surfaces and harmonic oscillator wave functions but includes differences in frequencies and reorganizational energies between the initial and final states, which is the crucial feature for the definition of an entropic change. Complications appear in the relationships that exist between optical and thermal electron transfer, and they are presented and discussed.

Introduction

In mixed-valence complexes, low-energy absorption bands often appear whose transitions, eq 1.1 (pz = pyrazine; bpy = 2,2'-bipyridine; (a) L = NH_3 ; (b) L = pyridine), are the photochemical



analog of the corresponding thermal electron transfers.²⁻⁵ Similarly, in excited-state decay, e.g., eq 1.2,⁶ emission is the analog of nonradiative decay. For either, the spectral profiles contain information about the analogous nonradiative process^{7,8} and have been used to calculate absolute or relative rate constants.^{6,9}

The quantities that are common to the optical and thermal processes and allow them to be interrelated are as follows: the energy difference between the reactants and products, changes in equilibrium displacements and frequencies of the vibrational modes, and changes in displacements and frequencies in the phonon or librational modes. Basic energy relationships can be easily derived based on harmonic potential energy functions as illustrated by the one-dimensional projection in Figure 1A, which is drawn with the same force constants assumed for the initial and final states.² The energy difference between the minima of the two curves is the internal energy difference, ΔE° . The coordinate, q , pertains to one of the participating normal modes of the complete system including both vibrations and librations. The reorganizational energy, χ , is the energy required to displace the coordinates of the reactants from their equilibrium values to the equilibrium values of the products without a change in electronic state. It is the difference in energy between the minimum of the product surface and that point on the surface of the product which is aligned vertically above the minimum of the reactant surface, as shown in Figure 1A. The reorganizational energy is normally partitioned into contributions from the intramolecular (inner-sphere) vibrations, χ_i , and solvent (outer-sphere) contributions, χ_o . The latter arise from vibrations, phonons, librations, and/or polarizations in the solvent or surrounding medium. The total

reorganizational energy is given by $\chi = \chi_i + \chi_o$.

Optical electron transfer is shown as the vertical transition from the minimum of the reactant curve to the product curve in Figure 1. The energy of this transition, E_{op} , is readily determined by graphical means giving eq 1.3. The activation energy for thermal

$$E_{\text{op}} = \chi + \Delta E^\circ \quad (1.3)$$

electron transfer, E_{th} , is the difference in energy between the minimum of the reactant surface and the point where the product and reactant surfaces intersect. This quantity can also be determined readily by graphical means giving eq 1.4. These results

$$E_{\text{th}} = E_{\text{op}}^2/4\chi \quad (1.4)$$

are correct provided that the force constants for the vibrations or librations are the same in both states. Based on these energy relationships, application of time dependent perturbation theory or a simple activated complex approach provides an expression for the thermal electron-transfer rate constant, eq 1.5. In the result from time-dependent perturbation theory the constant C contains the electronic coupling matrix element which, in the limit of weak electronic coupling between the reactants, can be related to the intensity of the absorption band.⁸

$$k_{\text{et}} = C^2 \exp(-E_{\text{th}}/kT) = C^2 \exp(-E_{\text{op}}^2/4kT\chi) \quad (1.5)$$

The scheme used to derive these energy relationships is limited in scope, especially since it ignores any effects arising from the thermal population of the vibrational or librational modes. More rigorous approaches based on a quantum mechanical model and time-dependent perturbation theory have been presented.^{8,10-12} With the further assumption of the harmonic oscillator model for the vibrational wave functions, it can easily be demonstrated that eq 1.3 is still valid if E_{op} is defined as the maximum of the absorption band.⁸ In an extremely important result, Jortner et al.¹¹ have demonstrated that eqs 1.4 and 1.5 can be obtained as the high-temperature, classical limit of the quantum mechanical treatment, provided that there is no change in frequency between the vibrational modes of the reactants and products. The inclusion of thermal population factors does not, in and of itself, alter the results of the simple model discussed above.

There remains a troubling flaw in these results. As written, ΔE° , χ , and E_{th} are internal energy changes and, since pressure-volume changes can usually be ignored, they are simply

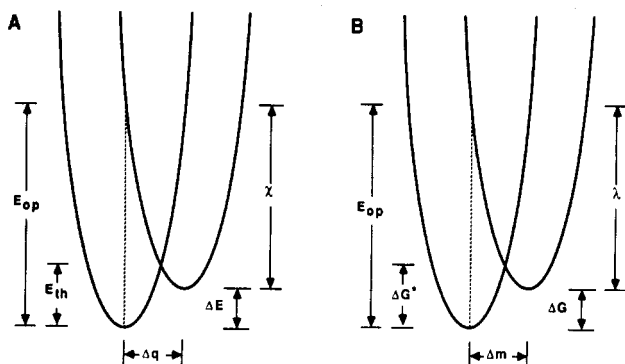


Figure 1. One-dimensional schematic energy diagrams illustrating the basic definitions and terms for thermal and optical electron transfer. The surfaces are assumed to be parabolic with the parabola on the left representing the reactants and the one on the right representing the products. The force constants for the reactants and products are taken to be the same. Electronic coupling at the intersection region is taken to be small and is ignored. A definition of the terms is given in the text. (A) Potential energy diagram used for the quantum mechanical approach. Energy quantities are enthalpies, and the coordinate q is a composite of the normal vibrational modes. (B) Free energy diagram used for the free energy surface approach. Energy quantities are free energies, and the coordinate m is the extent of electron transfer.

enthalpic quantities. By inference, E_{op} would also appear to be an enthalpic quantity. In this limited quantum mechanical formulation, it is not clear what role entropic or free energy contributions play, and this criticism has been raised in the literature.^{4,13} When changes in the frequencies of the vibrational modes between the reactants and products are taken into account, the quantities " E_{op} " and " E_{th} " derived from the quantum mechanical approach become temperature dependent.^{7,14,15} These energies would therefore appear not to be purely enthalpic quantities, but a more accurate description of their composition has not been derived.

An alternate approach for relating optical and thermal electron-transfer processes has been developed by Marcus and Sutin that is based on free energy surfaces.^{4,16} The foundation for this approach is the early, significant work of Marcus that demonstrated that the solvation energy of the activated complex (assuming a dielectric continuum model) depends quadratically on the extent of charge transfer.¹⁷ The extent of charge transfer, which was defined as the reaction coordinate, was assumed to remain in equilibrium with the polarization field of the surrounding solvent dipoles. With this approach, it was shown that the free energy surfaces for the reactants and products were quadratic with respect to the reaction coordinate. The results of this analysis are represented in the free energy diagram shown in Figure 1B, where ΔG° , λ , and ΔG^* are the free energy analogs of ΔE° , χ , and E_a , respectively. With the assumption of identical force constants for the surfaces of the reactants and products, relationships analogous to eqs 1.3–5 can be derived. They are given in eqs 1.6–8. These equations are more satisfactory in that they

$$E_{op} = \lambda + \Delta G^\circ \quad (1.6)$$

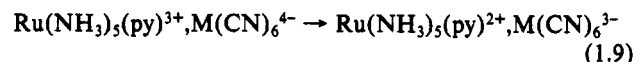
$$\Delta G^* = E_{op}^2 / 4\lambda \quad (1.7)$$

$$k_{et} = C^2 \exp(-\Delta G^* / kT) = C^2 \exp(-E_{op}^2 / 4kT\lambda) \quad (1.8)$$

incorporate free energies (and entropies, by inference). However, as was noted in their development and by others since,¹⁸ they are rigorously correct only when the reactant and product surfaces have identical force constants. Since the force constants of the reactants and products of an asymmetrical complex such as the one shown in eq 1.1 would, in general, not be the same, eqs 1.6–8 must be approximate solutions. In their application, however they are frequently treated as being general relationships. The incorporation of discrete, intramolecular vibrational modes into the free energy surface approach has been discussed, including development of the mathematics for frequency changes in the quantum modes,^{11–13} but the significance of this relative to the

enthalpy/free energy question was not addressed nor was the relaxation of the basic assumption of identical, parabolic free energy surfaces.

The differences between the quantum mechanical and free energy surface approaches need to be resolved, or at least, the assumptions that lead to the different results need to be delineated. In particular, there appears to be a conflict between these two approaches regarding the role of ΔG° and ΔE° , which experimentally, can be quite significant. For example, the entropic changes that accompany electron transfer within the ion pairs in eq 1.9 (py = pyridine, M = Fe, Ru, or Os) are quite large, +40 eu, which leads to a difference of 12 kcal/mol between ΔG° and ΔH° ($=\Delta E^\circ$) at room temperature.¹⁹ It is important to know



how these quantities can be derived from E_{op} and which quantities should be used in the expression for the rate constant. As another example, it has become common to estimate excited-state redox potentials by adding or subtracting such diverse quantities as ΔE° (the energy difference between the minima of the excited- and ground-state energy surfaces neglecting zero-point energy differences) or E_{em} (the emission band maximum) to or from the appropriate ground-state potential.²⁰ Since redox potentials provide a measure of free energy differences, these equations could only possibly be exact if ΔE° were derived rigorously from the spectroscopic data or if E_{em} were a free energy change.

Another point of interest is to develop a more complete model of the solvent and the role of entropy in electron transfer and nonradiative decay. For many mixed-valence systems, the dielectric continuum model developed by Marcus appears to describe adequately the role of the solvent, particularly for the optical process.^{3,5,21} For the ligand-bridged complex shown in eq 1.1b (L = pyridine), however, the optical transition shows a much stronger dependence on the solvent and the transition energy correlates very well with the donor number (DN) of the solvent,²² an empirical scale developed by Gutmann to describe the ability of a solvent to act as an electron pair donor (hydrogen-bond acceptor).²³ This has been attributed to strong hydrogen-bonding interactions between the NH_3 ligands and the solvent. It was further demonstrated that both ΔG° and the reorganizational energy of the complex depended upon DN. Another interesting aspect of this behavior is the existence of preferential solvation effects in mixed solvents.²⁴ For other mixed-valence complexes where the dielectric continuum model appears to be appropriate for most solvents, the behavior in water or other strongly hydrogen-bonding solvents can be anomalous.²⁵ The effects of related, specific solute-solvent interactions on charge-transfer transition energies are well known.²⁶

A related effect comes from the work of Weaver et al., where numerous entropies of reaction for electron transfer between metal complexes in solution and between metal complexes and an electrode have been measured.^{18,27,28} One general conclusion of that work is that entropies of reaction tend to be twice as large as those predicted by the Marcus model which is based on dielectric continuum theory.¹⁸ Further, it was found that the contribution to the entropic change by a particular solvent depended on the Gutmann acceptor number (AN) of the solvent,²³ a quantity that measures the ability of the solvent to act as an electron pair acceptor (hydrogen-bond donor). This contribution was significant even when the electroactive solute had no apparent basis for forming strong hydrogen bonds (e.g., $\text{Ru}(\text{bpy})_3^{3+/2+}$). Since a large portion of the entropic change for many electron-transfer reactions arises from solvent contributions, this implies that the dielectric continuum model does not provide a complete description of the role of the solvent. This is an important result since it requires that a more complicated structural model for the solvent be devised which should include the discrete librational-orientation characteristics of the solvent, especially of those modes involved in hydrogen bonding.

To help address these questions and seeming discrepancies, we have adopted a simultaneous experimental and theoretical ap-

proach. Experimentally, the temperature dependence of E_{op} for the unsymmetrical mixed-valence complex shown in eq 1.1a ($L = NH_3$) has been measured. Because of the coordination asymmetry at the two sites and the electrochemical results of Weaver et al. on complexes that are structurally related,^{18,27} a considerable entropic change is expected to exist between the initial and final states. This entropic change has been estimated by temperature-dependent electrochemical measurements. If the energy quantity contained within E_{op} is a free energy difference, a substantial temperature dependence of E_{op} is predicted to exist with the result that $\delta E_{op}/\delta T = -\Delta S^\circ$. As discussed above, this result should be independent of the assumption of a dielectric continuum model for the solvent.

On the theoretical side, we have reexamined the formulations for optical bandshapes and thermal electron-transfer rate constants based on a quantum mechanical approach where frequency changes are taken into account. This approach necessitates using different force constants for the potential energy surfaces of the reactants and products so that the results can be as general as possible. With this more general approach, we are able to demonstrate that the quantum mechanical treatment also predicts that E_{op} should vary with ΔG° in the classical limit, not simply with ΔE° . This allows us to show that a certain level of agreement exists between the experimental results and models based either on a quantum mechanical approach or on free energy surfaces. However, the quantum mechanical treatment demonstrates certain limitations in the formulations relating optical and thermal electron transfer, particularly in systems with large entropic changes. The implications of these results for the calculation of excited-state redox potentials and nonradiative decay rate constants will be discussed elsewhere.

Experimental Section

Materials. Acetonitrile (Burdick and Jackson), methylene chloride (EM Science), methanol (Burdick and Jackson), methanol-*d* (Aldrich), and bromine (Fisher, ACS Reagent Grade) were all used as received. Propionitrile and butyronitrile (Aldrich, Gold Label) were purified by heating 50 mL of the solvent with 0.4 g of Na_2CO_3 and 0.6 g of $KMnO_4$ at $\approx 70^\circ C$ for 90 min. If the purple color of the permanganate had disappeared, another 0.6 g of $KMnO_4$ was added, and the mixture was heated for another 60 min. The solvent was then decanted and distilled under reduced pressure at or near room temperature. The middle 50% of the distillate was collected, stored under argon, and used within 5 days. Tetra-*n*-butylammonium hexafluorophosphate, $[N(n-Bu)_4](PF_6)$, was prepared from $[N(n-Bu)_4]Br$ (Aldrich) and HPF_6 (Aldrich) and recrystallized three times from ethanol. Tetraethylammonium perchlorate $[NEt_4](ClO_4)$, was prepared from $[NEt_4]Cl$ (Aldrich) and $HClO_4$ (Aldrich) and recrystallized three times from ethanol.

Complexes. The salts $[(bpy)_2ClRu(pz)Ru(NH_3)_5](PF_6)_3$,²⁹ $[(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5](PF_6)_4$ ($4,4'$ -bpy = $4,4'$ -bipyridine),^{21b} and $[(bpy)_2ClRu(pz)RuCl(bpy)_2](PF_6)_2$ ³⁰ were synthesized as described previously. The mixed-valence forms of the complexes were generated electrochemically as follows: 15 mg of the reduced $Ru^{II}-Ru^{II}$ form of the complex was added to the center compartment of a three-compartment cell which was charged with 0.1 M $[N(n-Bu)_4](PF_6)$ in acetonitrile. A sufficiently positive potential (+0.80–1.0 V versus SSCE to oxidize both Ru centers) was applied to the cell until the current had reached <3% of its original value and the color change indicated that the oxidation was essentially complete. The solution containing the $Ru^{III}-Ru^{III}$ form of the complex was removed by pipette from the cell compartment and added to another 15 mg of the $Ru^{II}-Ru^{II}$ form. The solution was stirred for 1 min and added to 50 mL of stirring CH_2Cl_2 . The desired complex precipitated from solution as the PF_6^- salt while the supporting electrolyte remained in solution. The mixed-valence salt was isolated by filtration, washed with CH_2Cl_2 , and dried in vacuo. Yields were close to quantitative, and the electronic spectral characteristics of the samples matched those of mixed-valence samples which had been prepared by redox titration. The mixed-valence forms of each were also prepared in situ by two methods. In the first, 0.5 equiv of Br_2 was added

to a solution containing the $Ru^{II}-Ru^{II}$ form of the complex. In the second, the $Ru^{II}-Ru^{II}$ form of the complex was oxidized by 1 equiv with controlled potential electrolysis. The electronic spectral properties of the samples were essentially the same as those of the isolated mixed-valence complexes.

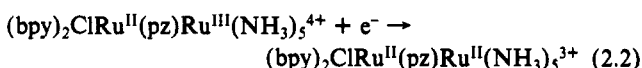
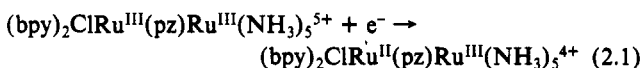
Measurements. Electronic spectra were recorded on a Cary 17I spectrophotometer. Temperature control of the sample cell was achieved by using an Oxford Instruments DN1704 liquid nitrogen dewar and No. 3120 temperature controller. The estimated accuracy of the temperature readout was $\pm 1^\circ C$. The reference cell was at room temperature. Solvent blank experiments at the lowest and highest temperatures confirmed that the temperature mismatch between the cells contributed negligibly to the baseline absorbance.

Variable temperature redox potential measurements were obtained by both cyclic voltammetry and differential pulse voltammetry by using a nonisothermal cell arrangement.³¹ The accuracy of the temperature measurement of the working compartment was $\pm 0.5^\circ C$. The working electrode was a gold wire. The reference was a saturated sodium calomel electrode (SSCE). The solvent was methanol with 35 mM $[NEt_4](ClO_4)$. The low ionic strength was required because of the limited solubility of the ClO_4^- salt of the complex. Controlled potential electrolysis was performed by using a Princeton Applied Research Model 173 potentiostat with current versus time traces recorded on a Hewlett-Packard Model 7015B X-Y recorder.

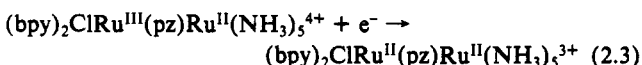
Results

In order to test whether eq 1.3 or 1.6 is valid, it is useful to find cases where the entropic difference between the states interrelated by the optical transition is maximized so that there is an appreciable difference between ΔG° and ΔH° . In solution, $\Delta H^\circ = \Delta E^\circ$ because the volume change is negligible. The temperature dependence of ΔG° , and therefore the entropic change, can be determined by variable temperature electrochemical measurements since $\delta \Delta G^\circ/\delta T = -\Delta S^\circ$. Provided that the temperature dependence of the reorganizational energy (λ or χ) can also be measured, a study of the temperature dependence of E_{op} should determine whether eq 1.3 or 1.6 is more appropriate. If eq 1.6 is correct, E_{op} should show the same temperature dependence as ΔG° , with $\delta E_{op}/\delta T = -\Delta S^\circ$. If eq 1.3 is correct, E_{op} should show very little dependence on temperature.

There is a considerable redox asymmetry in the complex in eq 1.1a ($L = NH_3$). It is induced by the difference in ligand environments and how those ligands interact with the solvent. From the known properties of complexes that are structurally related, the potential difference between the two types of couples, eqs 2.1 and 2.2, is considerable as is the manner in which the potentials respond to changes in temperature.²⁷ The $Ru^{II}(NH_3)_5^{2+}$ site is



the more strongly reducing of the two. It is oxidized at a lower potential as suggested by eq 2.2. The free energy change for eq 1.1 can be estimated from the difference in redox potentials as, ΔG° (eV) = $-\Delta E_{1/2} = [E_{1/2}(2.1) - E_{1/2}(2.2)]$. In this procedure the potential for eq 2.1 is used as an approximation for the potential of the corresponding $Ru(III/II)$ couple in the higher energy oxidation state isomer, eq 2.3. This is not entirely appropriate



because in this couple, reduction of $Ru(III)$ adjacent to $Ru^{III}(NH_3)_5$ occurs rather than reduction of $Ru(III)$ adjacent to $Ru^{II}(NH_3)_5$. The potentials for eqs 2.1 and 2.3 are expected to differ because of differences in electrostatic and electronic interaction terms. However, from the work of Schmitz on symmetrical, ligand-bridged complexes, these terms are expected to

TABLE I: Half-Wave Potentials from Cyclic and Differential Pulse Voltammetry as a Function of Temperature for the Couples $[(bpy)_2ClRu(pz)Ru(NH_3)_5]^{5+/4+/3+}$ in Methanol with 35 mM $[NEt_4](ClO_4)$ as the Supporting Electrolyte

T (°C)	$E_{1/2}(5+/4+)$	T (°C)	$E_{1/2}(4+/3+)$
-5.0	889	-2.5	410
-2.0	890	1.5	412
0.5	891	7.0	423
1.5	891	17.5	435
5.0	893	25.0	442
7.0	892	36.0	454
10.0	895	44.5	467
17.0	896		

^a The potentials, which were measured with a nonisothermal cell arrangement, are in mV versus an ambient temperature SSCE reference electrode.

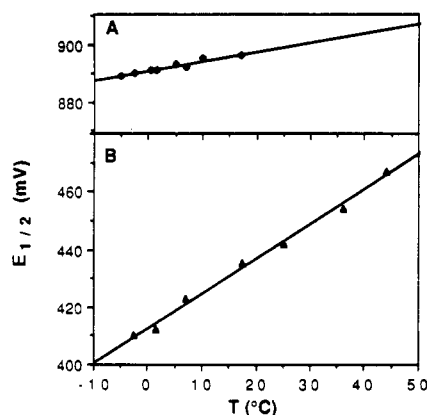


Figure 2. Temperature dependence of $E_{1/2}$ values (versus SSCE) for $[(bpy)_2ClRu(pz)Ru(NH_3)_5]^{3+}$ in CH_3OD with mM $[Et_4N][PF_6]$ for the following couples: (A) $[(bpy)_2ClRu^{III}(pz)Ru^{III}(NH_3)_5]^{5+/4+}$. (B) $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+/3+}$.

be temperature independent.³² Therefore, the temperature dependence of the difference in redox potentials corresponding to eqs 2.1 and 2.2 should be the same as those for the redox isomerization reaction in eq 1.1a.

The temperature dependences of the two redox couples in methanol were measured versus a room temperature SSCE and those data are given in Table I. Plots of the data are shown in Figure 2A and for reactions 2.1 and 2.2, respectively. The potentials of both couples exhibit a linear dependence on T with the slopes being $0.33 (\pm 0.10)$ and $1.20 (\pm 0.10)$ mV/°C for eqs 2.1 and 2.2, respectively. The much greater sensitivity to T for the $Ru(NH_3)_5$ based $Ru(III/II)$ couple is expected based on studies on related couples.^{18,27} It arises from the strong interactions of the ammine ligands with the solvent. The dependence of the difference in redox potentials ($\Delta E_{1/2}$) on T is also linear. From the experimental data, $\delta(\Delta E_{1/2})/\delta T = -0.9 \pm 0.2$ mV/°C. This is equivalent to a value of $\Delta S^{\circ} = +21 \pm 5$ eu ($\mu = 0.035$ M) for eq 1.1a.

The temperature dependence of the optical transition in eq 1.1a was examined in both CH_3OD and in 42:58 (v/v) propionitrile/*n*-butyronitrile solutions. Typical spectra are shown in Figure 3. They reveal that the peak maximum (E_{op}) is quite strongly temperature dependent. The spectra in CH_3OD were examined under three sets of conditions: (a) The isolated mixed-valence complex was added to pure solvent. (b) The reduced complex ($Ru^{II}-Ru^{II}$) was added to the solvent and oxidized by the addition of 0.5 equiv of Br_2 . (c) The reduced complex was added to CH_3OD containing 35 mM $[N(n-Bu)_4](PF_6)$ and oxidized electrochemically to the mixed-valence form. The data for the variation of E_{op} with T under these three conditions are collected in Table II. Plots of E_{op} versus T for the data are shown in Figure 4A. For each set of data E_{op} varies linearly with T although the correlations are independent of one another. The slopes of the linear least squares fits are -12 , -10 , and $-8 (\pm 2)$ cm⁻¹/°C for a, b, and c, respectively. These are equivalent to entropic changes of 34, 29, and 24 (± 6)

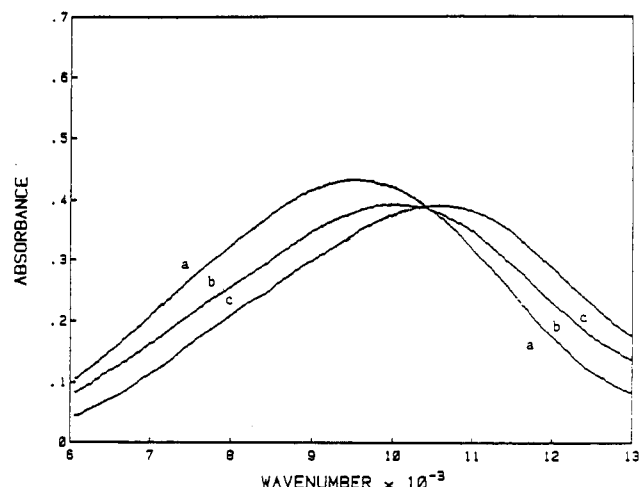


Figure 3. Temperature dependence of the intervalence transfer band in $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ in 7:9 propionitrile/butyronitrile at (a) 296 K, (b) 258 K, and (c) 209 K.

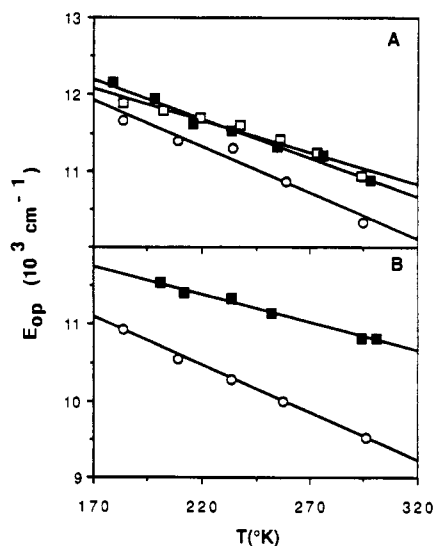


Figure 4. Plot of E_{op} versus temperature for $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ (A) in CH_3OD and (B) in 7:9 propionitrile/butyronitrile. Data points are for the following: O = mixed-valence complex in the solvent or solvent mixture; ■ = mixed-valence complex generated in solution by the addition of Br_2 ; □ = mixed-valence complex generated by electrochemical oxidation in the presence of 25 mM $[N(n-Bu)_4][PF_6]$. The drawn lines are the linear least squares best fits.

TABLE II: Temperature Dependence of the Band Maximum (E_{op}) of the Intervalence Transfer Band of $(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5^{4+}$ in CH_3OD under Various Conditions

T (K)	E_{op}^a (10^3 cm ⁻¹)	T (K)	E_{op}^b (10^3 cm ⁻¹)	T (K)	E_{op}^c (10^3 cm ⁻¹)
295	10.32	298	10.88	294	10.94
260	10.88	294	10.94	274	11.23
234	11.32	275	11.20	256	11.39
209	11.41	255	11.30	238	11.61
184	11.68	234	11.52	220	11.68
		215	11.60	202	11.79
		198	11.95	184	11.90
		179	12.16		

^a Mixed-valence complex isolated and added to neat solvent.

^b Mixed-valence complex generated in situ from the 3+ complex by the addition of Br_2 . ^c Mixed-valence complex generated in situ from the 3+ complex electrochemically with 25 mM $[N(n-Bu)_4](PF_6)$ present.

eu, respectively. The spectra in 42:58 (v/v) propionitrile/butyronitrile were examined under conditions a and b. These data are presented in Table III, and plots are shown in Figure 4B. Again, two independent linear correlations were found with slopes of -13 and $-7 (\pm 2)$ cm⁻¹/°C for a and b, respectively. These

TABLE III: Temperature Dependence of the Band Maximum (E_{op}) of the Intervalence Transfer Band of $[(bpy)_2ClRu^{II}(pz)Ru^{III}(NH_3)_5]^{4+}$ in 42:58 (ν/ν) *n*-Propionitrile/*n*-Butyronitrile

T (K)	E_{op}^a (10^3 cm $^{-1}$)	T (K)	E_{op}^b (10^3 cm $^{-1}$)
296	9.53	301	10.82
258	10.00	294	10.82
234	10.30	252	11.14
209	10.57	234	11.34
184	10.95	212	11.40
		201	11.54

^a Mixed-valence complex isolated and added to neat solution.

^b Mixed-valence complex generated in situ from the 3+ complex by the addition of Br $_2$.

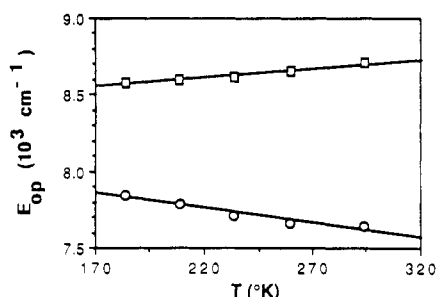
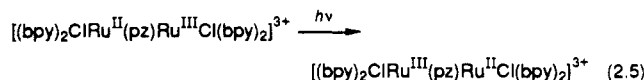
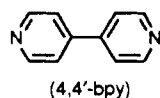
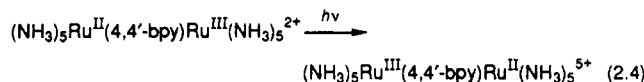


Figure 5. Plot of E_{op} versus temperature in 7:9 propionitrile/butyronitrile for $[(NH_3)_5Ru^{III}(4,4'-bpy)Ru^{II}(NH_3)_5]^{3+}$ (□) and for $[(bpy)_2ClRu^{II}(pz)Ru^{III}(bpy)_2]^{3+}$ (○).

correspond to entropic changes of 36 and 21 (± 6) eu, respectively.

Although a part of the analysis remains to be presented, the considerable temperature dependence of E_{op} clearly suggests a strong entropic component. Further, this contribution depends upon the counterions and the ionic strength of the solution. The counterion effect is particularly striking in comparing conditions a and b, which corresponds to replacing one of the four PF $_6^-$ counterions by Br $^-$. This testifies to the strong ion-pairing effects typically found for the smaller halide ions compared to bulkier counterions such as PF $_6^-$. The reduction in the magnitude of the entropic change in this case may have two somewhat related origins. First, tight ion pairing between the counterion and complex effectively increases the size of the complex by displacing some of the solvent molecules from the first solvent shell. Second, tight ion pairing decreases the effective charge of the complex. Both of these effects have been demonstrated to result in a decrease in the magnitude of the entropic changes associated with electron-transfer reactions.²⁷ The increase in ionic strength has the same effect because it also results in increased ion pairing.

In order to complete the analysis, the temperature dependence of the reorganizational energy must also be measured. It can be obtained by temperature dependent measurements on the component, symmetrical complexes, eqs 2.4 and 2.5. For a sym-



metrical complex, E_{op} should be equal to the reorganizational energy (λ or χ). Plots of E_{op} versus T in the nitrile mixture are shown in Figure 5. The slopes of the least squares correlations in Figure 5 are +1 (± 1) cm $^{-1}$ /°C for eq 2.4 and -2 (± 1) cm $^{-1}$ /°C for eq 2.5. When converted to entropic units, these correspond to changes of -3 (± 3) and +5 (± 3) eu for eqs 2.4 and 2.5, respectively.

The temperature dependences of the reorganizational energies for the reactions in eqs 2.4 and 2.5 arise from contributions by each of the two subunits. From the average of the two, the temperature dependence of the reorganizational energy for eq 1.1a can be estimated to be -1 (± 2) cm $^{-1}$ /°C, which corresponds to an entropic change of 3 (± 6) eu. This is only an approximate value because the reorganizational energies of each subunit depend, somewhat, on the complex that is attached to the other end of the bridge.

From eq 1.6, it is predicted that the temperature dependence of E_{op} should be equal to the sum of the temperature dependences of ΔG° and the reorganizational energy:

$$(\delta E_{op}/\delta T) = (\delta \Delta G^\circ/\delta T) + (\delta \lambda/\delta T) \quad (2.6)$$

The sum of these (21 (± 5) in CH $_3$ OD at $\mu = 0.035$ M and 3 (± 6) eu in the nitrile mixture, respectively) is within experimental error of $(\delta E_{op}/\delta T) = 29 \pm 4$ eu for eq 1.1a (CH $_3$ OD at $\mu = 0.025$ M). Although the spectral data were acquired in different solvents, the errors resulting for temperature-dependent studies in these different solvents should be small.^{18,27}

Theory

The experimental results suggest that E_{op} contains the free energy quantity ΔG° as in eq 1.6 rather than ΔE° as in eq 1.3. However, as was noted above, eq 1.3 was derived within the harmonic oscillator approximation with no frequency changes included. When frequency changes are taken into account, the formulations of absorption bandshapes give slightly different results. These will now be examined to determine if they are consistent with eq 1.6 as the results of the experimental work imply that they should be.

The methods for analyzing optical bandshapes are based on the use of generating functions developed by Kubo⁷ and the method of moments developed by Lax.³³ The results for systems involving frequency changes have been presented by several authors,^{8,14,34} and these are recapitulated here in a consistent notation. The Franck-Condon intensity distribution of an absorption band, $I(E)$, can be expressed as a Fourier transform integral as shown in eq 3.1,

$$I(E) = (d^2/2\pi\hbar) \int_{-\infty}^{\infty} \exp\left[f(t) + [\Delta E - E] \frac{it}{\hbar}\right] dt \quad (3.1)$$

where it is assumed that the transition moment integral, d^2 , is independent of energy. Here, ΔE is the difference in energy between the minima of the excited- and ground-state potential energy surfaces and $f(t)$ is the generating function for the vibrational wave functions. For harmonic oscillators with frequency changes at nonzero temperatures, the definition of $f(t)$ is given in eqs 3.2-4.

$$f(t) = \sum_j [B_j(t) - (1/2)\ln[A_j(t)]] - \Gamma^2 t^2 \quad (3.2)$$

$$A_j(t) = \left[2 \cosh(it\omega_j + \beta_j) \cosh(it\omega'_j) - \left[\frac{\omega_j^2 + \omega_j'^2}{\omega_j\omega_j'} \right] \times \sinh(it\omega_j + \beta_j) \sinh(it\omega'_j) - 2 \right] / [4 \sinh^2(\beta_j/2)] \quad (3.3)$$

$$B_j(t) = \frac{-(\omega_j\omega'_j/\hbar)(\Delta q_j)^2}{\omega_j \coth\left[\frac{it\omega_j + \beta_j}{2}\right] - \omega'_j \coth\left[\frac{it\omega'_j}{2}\right]} \quad (3.4)$$

Here, ω_j and ω'_j are the frequencies of mode j in the initial and final states, respectively, Δq_j is the displacement between the minima of the initial- and final-state surfaces along the mass-weighted normal coordinate j (units of g $^{1/2}$ cm), and $\beta_j = \hbar\omega_j/kT$. The term $-\Gamma^2 t^2$ on the right-hand side of eq 3.2 arises from representing the individual vibronic peaks as Gaussians whose full

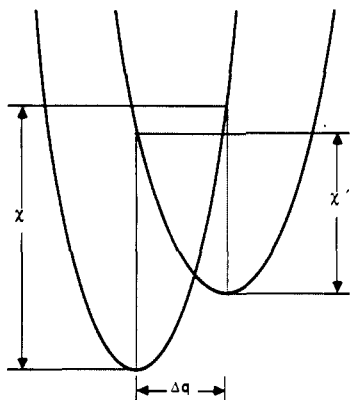


Figure 6. Potential energy diagram for the case where the reactant and product surfaces have different force constants. The reorganizational energy of the surface for the reactant is χ while that for the surface of the product is χ' . The vertical transition from the minimum of the reactant surface to the product surface has the energy $\Delta E + \chi'$.

width at half-maximum (fwhm) is given by $\text{fwhm} = \hbar \Gamma (16 \ln 2)^{1/2}$.

The various moments of the absorption band can be defined in terms of the derivatives of the generating function f , and the results for the first three moments are given in eqs 3.5–7. The

$$M_1 = \Delta E - i\hbar f'(0) = \Delta E + \sum_j \chi_j' + (\frac{1}{2}) \sum_j \hbar \Omega_j \coth(\beta_j/2) \quad (3.5)$$

$$M_2 = -\hbar^2 f''(0) = \sum_j \frac{(\hbar \omega_j')^2}{\hbar \omega_j} \chi_j' \coth(\beta_j/2) + (\frac{1}{2}) \sum_j (\hbar \Omega_j)^2 \coth^2(\beta_j/2) + 2\hbar^2 T^2 \quad (3.6)$$

$$M_3 = i\hbar^3 f'''(0) = \sum_j (\hbar \Omega_j)^2 \coth(\beta_j/2) [\hbar \omega_j + \hbar \Omega_j \coth^2(\beta_j/2)] + \sum_j \chi_j' (\hbar \omega_j')^2 \left[1 + 3 \frac{\hbar \Omega_j}{\hbar \omega_j} \coth^2(\beta_j/2) \right] \quad (3.7)$$

quantities $f'(0)$, $f''(0)$, and $f'''(0)$ are the values of the first, second, and third derivatives, respectively, of $f(t)$ evaluated at $t = 0$. The definitions of χ_j' and Ω_j are given in eqs 3.8 and 3.9, respectively.

$$\chi_j' = (\frac{1}{2})(\omega_j')^2 (\Delta q_j)^2 \quad (3.8)$$

$$\Omega_j = \frac{(\omega_j')^2 - (\omega_j)^2}{2\omega_j} \quad (3.9)$$

χ_j' is the reorganizational energy (defined above) in mode j along the final-state potential surface. The reorganizational energy in mode j along the potential surface of the initial state, χ_j , would differ by having ω_j^2 in place of $(\omega_j')^2$; i.e., the two quantities are not equal unless $\omega_j = \omega_j'$. These relationships are illustrated in Figure 6. The quantity Ω_j is seen to be nonzero for $\omega_j \neq \omega_j'$ and can be either positive or negative depending upon whether ω_j' is larger or smaller than ω_j .

The relationship of these moments to the absorption bandshape is straightforward. The first moment (M_1) is the average energy (mean) of the bandshape, the second moment (M_2) is the standard deviation (width) of the bandshape about its mean, and the third moment (M_3) measures the degree of skewing of the distribution about the mean. In room temperature, fluid solutions, most absorption bands for metal complexes tend toward Gaussian shapes. For such distributions, more direct interpretations of the band moments arise. M_1 becomes equivalent to the band maximum (E_{op}), and M_2 can be related to the full width at half-maximum ($\Delta\nu_{1/2}$) as shown in eq 3.10. The degree of skewing

$$M_2 = (\Delta\nu_{1/2})^2 / (8 \ln 2) \quad (3.10)$$

of the band is measured by the ratio $(M_3^2/M_2^3)^{1/2}$ which goes to

zero for a symmetrical bandshape. In the high-temperature, classical limit ($\hbar \omega_j \ll kT$), M_3 is not exactly zero. Rather, the second half of the second term in the right-hand side of eq 3.7 persists to give eq 3.11 in the classical limit. Thus, in order to obtain the "classical" Gaussian bandshape the additional assumption that $\hbar \Omega_j \ll \hbar \omega_j$ is required. This seemingly minor point has significant ramifications for later arguments.

$$M_3 = 3(2kT)^2 \sum_j \chi_j' \left(\frac{\hbar \omega_j'}{\hbar \omega_j} \right)^2 \frac{\hbar \Omega_j}{\hbar \omega_j} \quad (3.11)$$

As has been noted previously,^{7,8,11–13} eq 3.5 reduces to eq 1.3 for the case of no changes in frequency between the initial and final states ($\Omega_j = 0$) in the classical limit. For the case where frequency changes do occur ($\Omega_j \neq 0$), eq 3.5 predicts that E_{op} ($=M_1$) will be temperature dependent and that eq 1.3 is not, in general, correct. Since it has been demonstrated here on experimental grounds that E_{op} should be related to ΔG° , there is an implication that the last term on the right-hand side of eq 3.5 (which contains the temperature dependence) should be related to the entropic change.

The entropic content of an harmonic oscillator vibrational mode is readily defined³⁵ and can be rewritten in terms of hyperbolic trigonometric functions as shown in eq 3.12 where $\beta_j = \hbar \omega_j/kT$, as before. With some mathematical manipulations, the change

$$S_j/k = (\beta_j/2) \coth(\beta_j/2) - \ln [2 \sinh(\beta_j/2)] \quad (3.12)$$

in entropy in a particular vibrational mode (ΔS_j) that results because of a change in frequency can be expressed as in eq 3.13, where $\beta_j' = \hbar \omega_j'/kT$ and $\Delta\omega_j = \omega_j' - \omega_j$.

$$\Delta S_j/k = (\beta_j'/2) \coth(\beta_j'/2) - (\beta_j/2) \coth(\beta_j/2) - \ln [\cosh(\hbar \Delta\omega_j/2kT)] - \ln [1 + \tanh(\hbar \Delta\omega_j/2kT) \coth(\beta_j/2)] \quad (3.13)$$

For the high-temperature limit ($\hbar \omega_j'$ and $\hbar \omega_j \ll kT$) with small frequency changes ($\Delta\omega_j \ll \omega_j'$ and ω_j), it is found that the first two terms on the right-hand side of eq 3.13 almost exactly cancel and the third term is quite small. Only the fourth term on the right-hand side of eq 3.13 is of any consequence. That term can be further simplified with the approximations $\tanh(x) \approx x$ and $\ln(1+x) \approx x$ for small x to give the result shown in eq 3.14.

$$\Delta S_j/k \approx -(\hbar \Delta\omega_j/2kT) \coth(\beta_j/2) \quad (3.14)$$

Finally, since $\Omega_j \approx \Delta\omega_j$ for small $\Delta\omega_j$ the desired relationship between entropy and the third term on the right-hand side of eq 3.5 is accurately expressed by eq 3.15.

$$T\Delta S \approx -(\frac{1}{2}) \sum_j \hbar \Omega_j \coth(\beta_j/2) \quad (3.15)$$

The physical significance of this term can be made more transparent by including the high-temperature limit of $\coth(\hbar \omega_j/2kT) \approx 2kT/\hbar \omega_j$ in eq 3.14 to give the result in eq 3.16.

$$T\Delta S \approx -kT \sum_j \frac{\hbar \Delta\omega_j}{\hbar \omega_j} \quad (3.16)$$

This shows that the entropic change in a particular vibrational mode is proportional to the relative frequency change in that mode. If the frequency of the mode increases upon change of electronic state, its contribution to the entropic change is negative and vice versa. This result is obtained because the increased vibrational spacing decreases the number of vibrational states that are thermally accessible at a particular temperature. It is interesting to note that a proper combination of modes, some increasing and some decreasing in frequency, could result in no net entropic change despite large changes in individual frequencies.

Give the approximation that $E_{\text{op}} \approx M_1$, eqs 3.5 and 3.15 give the result shown in eq 3.17. Since there should be negligible

$$E_{\text{op}} = \Delta E^\circ + \sum_j \chi_j - T\Delta S^\circ = \Delta G^\circ + \sum_j \chi_j \quad (3.17)$$

pressure-volume work, $\Delta E^\circ = \Delta H^\circ$ and $\Delta G^\circ = \Delta E^\circ - T\Delta S^\circ$ so that a linear relationship between E_{op} and ΔG° exists as shown

TABLE IV: Comparison between the Exact Entropic Change (ΔS) Calculated by using Eq 3.13 and the Two Approximate Entropic Changes Calculated by using Eq 3.14 ($\Delta S_{\Delta\omega}$) and Eq 3.15 (ΔS_{Ω}) for Various Combinations of Vibrational Spacings at $kT = 200 \text{ cm}^{-1}$

$\hbar\omega \text{ (cm}^{-1}\text{)}$	$\hbar\omega' \text{ (cm}^{-1}\text{)}$	$\Delta S/k$	$\Delta S_{\Delta\omega}/k$	$\Delta S_{\Omega}/k$
30	15	0.692	0.501	0.376
30	21	0.356	0.301	0.255
30	27	0.105	0.100	0.095
30	33	-0.095	-0.100	-0.105
30	39	-0.262	-0.301	-0.346
30	45	-0.404	-0.501	-0.626
300	150	0.627	0.590	0.443
300	210	0.313	0.354	0.301
300	270	0.089	0.118	0.112
300	330	-0.078	-0.118	-0.124
300	390	-0.206	-0.354	-0.407
300	450	-0.307	-0.590	-0.738

in eq 3.17. It should be recalled that the approximation that $E_{\text{op}} \approx M_1$ relied on M_3 being small. This in turn required that $\hbar\Omega_j \ll \hbar\omega_j$ which also necessitates small entropic changes. This is a noteworthy limitation on the results of the analysis. There is an additional, significant difference between eqs 1.6 and 3.17. Equation 3.17 only involves the *enthalpic* reorganizational energy (χ), which has been defined relative to the potential energy surface, whereas eq 1.6 involves the reorganizational *free* energy (λ). This quantity has yet to be defined in the present context. These points will be discussed in more detail below. The conclusion that we wish to emphasize here is that, starting with simple, temperature-independent potential energy surfaces and by using the quantum mechanical approach, an expression can be derived in a direct manner which involves free energies and not just enthalpies. This shows that this approach is more general than previous criticisms have allowed.

The validity of the approximations used to derive eq 3.15 are illustrated by the results of calculations presented in Table IV and by the plots in Figure 7. In the plots, the exact result for the entropic change calculated by using eq 3.13 (ΔS) is compared with the results calculated by using the approximate forms shown in eq 3.14 ($\Delta S_{\Delta\omega}$) and eq 3.15 (ΔS_{Ω}) over the range $\hbar\omega = 1\text{--}1000 \text{ cm}^{-1}$ for $kT = 200 \text{ cm}^{-1}$. Selected calculated values are presented in Table IV. Four sets of curves are shown in the figure for values of $\Delta\omega/\omega = -0.3, -0.1, +0.1, \text{ and } +0.3$ from top to bottom, respectively.

The first noteworthy point to emerge from the comparisons is that the results for $\hbar\omega = 100 \text{ cm}^{-1}$ are indistinguishable from those for $\hbar\omega = 1 \text{ cm}^{-1}$. This demonstrates the range of modes that can be treated "classically" in this respect. Even the greatly simplified result calculated by using eq 3.16 is in good agreement for $\hbar\omega \leq 100 \text{ cm}^{-1}$. It is not until $\hbar\omega > 300 \text{ cm}^{-1}$ that the thermal population of vibrationally excited states is sufficiently small that the entropic contribution is severely diminished by thermal factors. A second point is that the two approximate formulas are in excellent agreement with the exact result for $\Delta\omega/\omega = \pm 0.1$ and $\hbar\omega < 300 \text{ cm}^{-1}$. There is a marked divergence between the two results for $\hbar\omega > 300 \text{ cm}^{-1}$. This is of little concern since the entropic contributions from such modes are negligible. The level of agreement is much less satisfactory for larger relative changes in frequency. In the case of $\Delta\omega/\omega = \pm 0.3$, for example, eq 3.14 is in error by 15–20% and eq 3.15 is in error by 30% in representing the entropic changes. This is a point of concern since it is not known what the magnitudes are for frequency changes (or effective changes) in the librational or phonon modes that accompany electron transfer. We suspect that, in most cases (particularly for inner-sphere modes and solvent modes involving hydrogen-bonding or strong polar interactions), these will be less than 30% but that exceptions will certainly arise. The quantum mechanical treatment shows that eq 3.17 is approximately true, probably to a good level of accuracy. However, the exact equality that is obtained in the free energy surface approach does not emerge, at least directly, at this level of treatment.

The formulation of the thermal electron-transfer rate constant by this approach involves essentially the same mathematics.^{7,8,11,12}

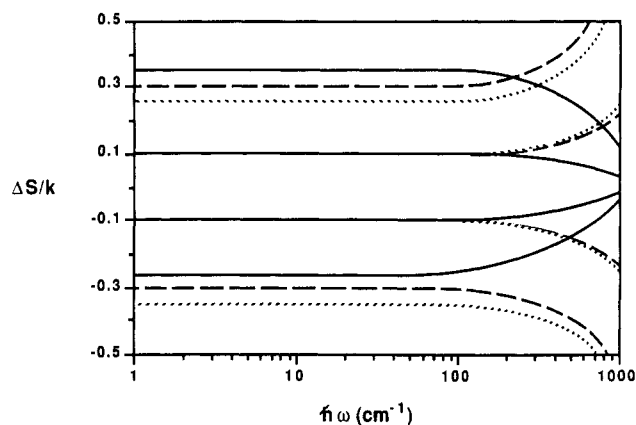


Figure 7. Comparison of calculated entropic changes as a function of frequency for $kT = 200 \text{ cm}^{-1}$. Results are shown for the exact entropic change, ΔS , calculated by using eq 3.13 (—), the first approximate entropic change, $\Delta S_{\Delta\omega}$, calculated by using eq 3.14 (---), and the second approximate entropic change, ΔS_{Ω} , calculated by using eq 3.15 (···). Four sets of three curves are shown which correspond, from top to bottom, to frequency changes of -30%, -10%, +10%, and +30%, respectively.

The rate equation can be expressed by the Fourier transform integral shown in eq 3.18

$$k_{\text{et}} = \frac{V^2}{\hbar^2} \int_{-\infty}^{\infty} \exp[f(t) - it\Delta E/\hbar] dt \quad (3.18)$$

where k_{et} is the thermal electron transfer rate constant, V contains the electronic coupling matrix element (assumed to be independent of energy and coordinates), and $f(t)$ is the generating function defined in eqs 3.2–4. Although the exact integral can be readily evaluated by numerical techniques, it is useful to obtain an approximate formulation. For this, the Taylor series expansion for $f(t)$ about $t = 0$ as shown in eq 3.19 is utilized, where the first three derivatives were defined in eqs 3.5–7. By neglecting terms

$$f(t) = f(0) + f'(0)t + f''(0)t^2/2 + f'''(0)t^3/6 + \dots \quad (3.19)$$

of t^3 and higher orders (which is the high-temperature, classical approximation with the additional constraint that $\hbar\Omega_j \ll \hbar\omega_j$ so that M_3 is sufficiently small), the integral can be solved in closed form giving the result shown in eq 3.20. (The saddle point method

$$k_{\text{et}} = \frac{V^2}{\hbar} \left(-\frac{2\pi}{\hbar^2 f''(0)} \right)^{1/2} \exp \left[\frac{[\Delta E - i\hbar f'(0)]^2}{2\hbar^2 f''(0)} \right] = \frac{V^2}{\hbar} \left(\frac{2\pi}{M_2} \right)^{1/2} \exp \left[-\frac{[M_1]^2}{2M_2} \right] \quad (3.20)$$

of ref 11 can also be used to obtain the same result, but the mathematics are more tedious.) The thermal rate constant is found to be a simple function of the band moments of the optical process under these approximations. As noted above, M_1 and M_2 can be related to the band maximum (E_{op}) and full width at half-maximum ($\Delta\nu_{1/2}$) in the high-temperature, classical limit. The resulting relationship between the optical and thermal processes is given in eq 3.21. This simple relationship between optical and thermal parameters has been derived previously by several workers by using different approaches.

$$k_{\text{et}} = \frac{V^2}{\hbar} \left(\frac{16\pi \ln 2}{(\Delta\nu_{1/2})^2} \right)^{1/2} \exp \left[-\frac{4 \ln 2 (E_{\text{op}})^2}{(\Delta\nu_{1/2})^2} \right] \quad (3.21)$$

It is desirable to write this formulation in terms of thermodynamic functions as was previously done for E_{op} (eq 3.17). This requires deriving a thermodynamic expression for M_2 (eq 3.6), which cannot be achieved as cleanly as it could for E_{op} . First, it must be assumed that the high-temperature limit applies so that $\coth(\beta/2) \approx 2kT/\hbar\omega$ which leads to eq 3.22. To simplify

$$M_2 = 2kT \sum_j \chi_j' \frac{(\hbar\omega_j)^2}{(\hbar\omega_j)^2} + 2kT \sum_j kT \frac{(\hbar\Omega_j)^2}{(\hbar\omega_j)^2} \quad (3.22)$$

further, it must first be assumed that $\sum(\Delta\omega_j/\omega_j)^2 \ll \sum(\chi_j'/kT)$ so that the second term on the right-hand side can be neglected. This condition fails for certain vibrational modes for which $\chi_j' \ll kT$, but the summation over all vibrational modes makes it very likely that this relationship holds in general. It must also be assumed that $\hbar\omega_j'/\hbar\omega_j \approx 1$ so that the first term can be simplified to give the result in eq 3.23. The latter assumption is tantamount

$$M_2 = 2kT \sum_j \chi_j' \quad (3.23)$$

to the approximation $\chi_j \approx \chi_j'$ which implies small entropic changes in those modes which contribute to the reorganizational energy. Substitution of eqs 3.23 and 3.17 into eq 3.21 gives the desired result in eq 3.24. This result is similar to eqs 1.6–8 in that it

$$k_{et} = \frac{V^2}{\hbar} \left(\frac{\pi}{kT \chi'} \right)^{1/2} \exp \left[-\frac{(\Delta G + \chi')^2}{4kT \chi'} \right] \quad (3.24)$$

is cast in terms of the free energy change ΔG° rather than ΔE° as in eqs 1.3–5. This shows that the quantum mechanical approach based on simple potential energy surfaces, once again, results in useful expressions that involve free energies once frequency changes are taken into account. In the definition of E_{op} in eq 3.17, eq 3.24 involves the reorganizational enthalpy (χ) rather than the reorganizational free energy (λ) that appears in eqs 1.6–8. As with eq 3.17, the approximations required to obtain eq 3.24 suggest that it is not exactly valid for reactions with large entropic changes.

Discussion

A significant temperature dependence exists in the energy of the intervalence transfer band for the unsymmetrical complex in eq 1.1a with E_{op} decreasing as the temperature increases: $(\delta E_{op}/\delta T) = -10 \text{ cm}^{-1} \text{ K}^{-1}$ or $+29 \pm 6 \text{ eu}$ in CH_3OD , $\mu = 0.035 \text{ M}$. From both the free energy surface approach and the quantum mechanical treatment presented here, this quantity should represent (at least to first order) the temperature dependence of $\Delta G^\circ + (\lambda \text{ or } \chi)$. The temperature dependence of ΔG° could be reliably derived from the electrochemical measurements ($\Delta S^\circ = +21 \pm 5 \text{ eu}$, CH_3OD , $\mu = 0.035 \text{ M}$), where the relatively large temperature dependence (see, for example, refs 18, 27, and 31) minimizes experimental complications. (The actual thermodynamic quantities measured in the experiments are ΔS° and ΔG° rather than ΔS° or ΔG° since the measurements were made under nonideal conditions.) The temperature dependence of λ or χ was evaluated from the temperature dependences of eqs 2.4 and 2.5 and was found to be small $+3 \pm 6 \text{ eu}$. Within experimental error, the temperature dependences of E_{op} and $\Delta G + (\lambda \text{ or } \chi)$ are indistinguishable, with both being large quantities. From this observation, it can be inferred that E_{op} must depend on ΔG° for the intramolecular electron-transfer reaction. That is to say, either eq 1.6 or 3.17 could be correct, but eq 1.3 is not correct.

The entropic changes for many electron-transfer reactions appear to originate largely in the solvent.²⁷ The large positive entropic change found here suggests a considerable decrease in "electrostriction" when the electron is transferred across the ligand bridge. This is consistent with two distinct results of the electron-transfer act. First, the overall charge distribution in the complex (viewed as two neighboring redox sites) is made more symmetrical in the conversion from the starting distribution (3+,1+) to the final distribution (2+,2+). Second, the positive charge is transferred from the relatively compact ammine site ($r \approx 4.2 \text{ \AA}$) to the larger bpy site ($r \approx 6.5 \text{ \AA}$). Both of these effects reduce the total strength of the electric field that the solvent senses and decrease the order imposed on the solvent. Alternatively, this can be viewed as a decrease in the effective force constant for the librational modes by which the solvent dipoles are ordered. This results in a decrease in quantum spacings and an increase in the number of quantum levels for the librational modes that are thermally populated. The net result is that the entropy of the system increases. The effects of both charge and size on the solvation entropy for electron-transfer reactions have been demonstrated experimentally for related, nonbridged complexes.²⁷

In agreement with these experimental results, we have shown that the quantum mechanical treatment also gives the result that E_{op} depends on ΔG° in the classical limit. Thus, this result appears to be independent of the assumption of either a dielectric continuum for the solvent or a derivation based on free energy surfaces. The long-standing disagreement over this point now seems to be resolved. Given the disparate approaches taken by the two treatments, there is a strong suggestion that this conclusion is general for all types of low-frequency modes (librational, lattice, or internal) independent of whether or not the modes are harmonic, *as long as the modes are near the classical limit*. The quantum treatment points to two limitations in the relationship between E_{op} and ΔG° which are not so readily apparent in previous treatments. One is the distinction between the band maximum and the mean band energy (E_{op} versus M_1), and the other is the restriction to relatively small frequency changes ($\Delta\omega/\omega \ll 1$).

There is no inherent difficulty in defining or incorporating the effects of free energy within a quantum mechanical treatment. That result arises directly from the inclusion of frequency changes and the definition of the entropic content of an harmonic oscillator. Previous quantum treatments have usually assumed the equivalence of internal and free energy changes without attempting to define the role of entropy or have defined the entropic change based on the classical dielectrical continuum model of the solvent described by Marcus.^{10,13} Our results remove this inaccuracy and provide a transition between the two treatments.

The two may differ regarding the assumption of equivalent force constants. There is a strong suggestion from the present results that any analysis that does not include different force constants for products and reactants in an asymmetrical system cannot include all entropic effects accurately. This is certainly true for the quantum treatment. Thus it is unclear how best to extrapolate the "general" relationships presented in the Introduction to asymmetrical systems. Other points that arise in the quantum mechanical/free energy surface comparison are the distinction between enthalpic and free reorganizational energies (χ versus λ), and the effects of anharmonic and temperature dependent potential surfaces.

Before developing these points further, it should be emphasized that the major goal of this manuscript is the analysis of optical electron transfer and its relationship to the corresponding thermal electron transfer. Optical electron transfer is rapid compared to vibrational or librational processes so that all such motions are treated as slow compared to the optical transition. Conversely, a major assumption in the derivation of the thermal rate equation is that thermal electron transfer is slow compared to vibrational and librational motions (and the maintenance of thermally equilibrated distributions), and all such motions are treated as being rapid compared to the thermal transition. The optical process can provide no distinction between differences in thermal electron transfer and vibrational/librational timescales. Thermal rate constants from optical parameters will be directly applicable only for systems where there are no complications from dynamical solvent behavior. The influence of dynamical solvent behavior is an important issue in its own right, and several approaches to incorporate dynamical effects, by stochastic or semiclassical analyses, or by molecular dynamics simulations, have been developed.^{36–38} The results of our analysis are restricted to cases where there are no important dynamical effects and are not general in this regard. For example, they do not apply to thermal rates which are comparable with frequencies for librational motions so that these motions become a dynamically determining factor.

Coupling of the current results with dynamical treatments is certainly possible and needs to be pursued, especially since the entropic contribution tends to be dominated by the solvent librational modes. The lack of thermal equilibration in these modes when electron transfer occurs will alter the effective entropy of activation. However, this is far beyond the scope of our current analysis.

The Quantum Treatment. The first important point that arises in the quantum treatment is the distinction between the band maximum, E_{op} , and the mean band energy, M_1 . The quantity E_{op}

is usually associated with the absorption maximum but bandshapes of typical intervalence transfer (IT) bands are noticeably asymmetrical with the high-energy side of the band broader (typically by at least a factor of 1.2) than the low-energy side.^{2,3,5,8} The first moment M_1 is defined in terms of the maximum in the Franck-Condon envelope. The absorption spectrum is the distribution in energy of the Franck-Condon overlap at some energy times that energy.¹⁵ Unweighted spectra are more symmetrical, and the apparent band maxima are shifted to lower energies (typically several hundred cm^{-1} for low-energy IT bands).^{39,40} The present treatment clearly shows that, for proper utilization of formulas 1.3–8, 3.17, and 3.21, E_{op} should be taken as the maximum of the Franck-Condon envelope rather than the absorbance maximum. This point has been made previously by Hush.^{2b,8}

This still leaves a distinction to be made between the band maximum and the mean band energy. For asymmetrical bandshapes, the band maximum is given approximately by $E_{\text{op}} = M_1 - M_3/2M_2$.⁴¹ In the classical limit the largest term defining $M_3/2M_2$ is $3kT(\sum \chi_j \Delta \omega_j / \omega_j) / (\sum \chi_j)$. The form of this term is reminiscent of an entropic contribution in that it could be described as the weighted average of the entropic change in the modes that contribute to the reorganizational energy multiplied by a factor of 3. The fact that the quantity is an average rather than a sum of entropic terms and the seemingly extraneous factor of 3 discourages any direct thermodynamic assignment to this term (such as the entropic portion of the reorganizational energy).⁴² For asymmetrical bandshapes we infer that M_1 is the quantity of interest rather than E_{op} . For harmonic modes in the classical limit, the distinction between E_{op} and M_1 would appear to be of no great concern. Assuming a value for $(\sum \chi_j \Delta \omega_j / \omega_j) / (\sum \chi_j)$ of 0.1, the difference between M_1 and E_{op} at room temperature would only be 60 cm^{-1} and the temperature dependence of the band maximum would change by 0.2 $\text{cm}^{-1} \text{K}^{-1}$. This value is negligible compared to the experimental result obtained for the mixed-valence complex but could be significant for other processes where the entropic change is smaller. The conditions $\hbar\omega \ll kT$ and $\Delta\omega/\omega \leq 0.1$ are stringently required for the relationship $M_1 = \Delta G^\circ + \chi$ to be valid so that in this limit $E_{\text{op}} = M_1$. For the more realistic case of anharmonic modes, M_3 would be larger in magnitude and the difference between E_{op} and M_1 would be greater. Further quantitative evaluation of this aspect is being pursued.⁴²

These limitations become more important for the evaluation of the thermal rate constant as evidenced by the difficulty encountered in the simplification of eq 3.20 to eq 3.24. The most restrictive step there was the derivation of eq 3.23 which required that $\omega/\omega' \approx 1$, which implies, at least, that $\Delta\omega/\omega \ll 1$. More importantly, for those modes with substantial values of χ reasonable numerical accuracy requires that $\Delta\omega/\omega < 0.1$. This is more restrictive than the assumption required for the simplification of M_1 . It implies that $\chi/\chi' \approx 1$ and that entropic changes must be small.

A related aspect appears in comparing rate constants for forward (k_{et}) and reverse (k_{et}') electron transfer. From thermodynamic reversibility, $k_{\text{et}}/k_{\text{et}}' = \exp(-\Delta G^\circ/kT)$. If eq 3.24 is utilized for k_{et} and k_{et}' , reversibility requires $\chi = \chi'$, and there is no entropic change. Even when the full second-order expression in eq 3.20 is utilized for k_{et} and k_{et}' and a second-order expansion for the entropic term is used, reversibility requires $\Delta\omega/\omega \ll 1$. This result is not surprising because in the classical limit M_3 is linearly dependent on $\Delta\omega/\omega$. Since $T\Delta S$ also depends on $\Delta\omega/\omega$, in this limit one cannot expect to account completely for entropy without including M_3 . The major difficulty arises from the differences between M_2 and M_2' which originate from the differences between χ and χ' . In fact, the quantities M_3 and M_3' contain the necessary information to resolve these problems, and higher order treatments are required to resolve these discrepancies.

Similar difficulties are encountered in attempting to apply simple classical treatments assuming Gaussian bandshapes to asymmetrical chemical systems. This is best illustrated by first considering the modifications required for eqs 1.6–1.8 under the conditions that $\lambda \neq \lambda'$. In this case, the free energy of activation

from eq 1.8 is given approximately by $\Delta G^\circ = (\lambda_a + \Delta G^\circ)^2/4\lambda_a$ where $\lambda_a = 2\lambda\lambda'/(\lambda + \lambda')$,^{17,18b} although the exact expression is much more complicated.⁴³ The value for E_{op} would still apparently be $E_{\text{op}} = \Delta G^\circ + \lambda'$, from which ΔG° could no longer be directly calculated since λ remains unknown. It would be necessary to measure the optical transition for the reverse process ($E_{\text{op}}' = \lambda - \Delta G^\circ$) to obtain this quantity. Thus, with $\lambda \neq \lambda'$ for the full inclusion of entropic effects, it does not seem possible to relate the optical and thermal processes in a simple way.

The relationships between the optical and thermal processes derived in the Kubo-Lax formulation assert that a complete description of one of the optical processes should provide a complete description of the thermal process.^{7,33} The second-order expansions utilized here do not contain all of the necessary information since they also imply that the optical transition for the reverse process is required in order to obtain values for both χ and χ' . We have continued the present derivation to third order by using the saddle point method. Those results will be presented in full detail elsewhere,⁴² but the pertinent conclusions for the current work are as follows: (1) The first band moment and band maximum still depend upon ΔG° . (2) Inclusion of the third moment does result in the satisfaction of the reversibility criterion. (3) The moments of one of the optical processes do contain sufficient information to calculate the forward and reverse rate constants, i.e., both χ and χ' are obtainable from one of the bandshapes. (4) The relationships between the rate constants and the thermodynamic quantities are rather complex in form but have simpler formulations in terms of the band moments.

The remaining distinction between the classical and quantum mechanical treatments is whether the reorganizational energy in these formulations is a free energy (as in eqs 1.6–8) or an enthalpy (as in eq 3.24). The origin of this discrepancy is probably in the assumption made here of harmonic, temperature-independent potential surfaces. The two important properties of the harmonic oscillator in this regard are that the average nuclear position always corresponds to the minimum of the enthalpic well, regardless of temperature, and that the frequency of the mode does not change as a function of either position on the potential surface or the temperature.

There are two simple ways by which a temperature dependence could be introduced into χ and χ' . The first would be to allow Δq to be temperature dependent, and the second to allow ω and ω' to be temperature dependent. The first is easier to analyze since it does not affect ΔG° . The extra temperature dependence introduced in this way would be attributable to the entropic portion of the reorganizational energy since ΔS° is unaffected. This second situation is more complicated since if ω and ω' are temperature dependent, ΔS° is also temperature dependent. In either case the values of $\Delta\omega$ or ω and ω' (and χ and χ') to use in formulations of optical or thermal electron transfer are those at the prevailing temperature and could probably be more properly described as λ , the reorganizational free energy.

A more realistic method for analyzing the distinction between λ and χ is probably through the introduction of anharmonic oscillators (e.g., Morse oscillators). The average nuclear displacement for the Morse oscillator does not directly correspond to the minimum of the potential surface for any finite temperature and is a function of temperature. The average shifts toward larger displacement as the temperature increases. Similarly, the Boltzmann averaged frequency of the mode will decrease as the temperature increases. In effect, the frequency of the mode depends on the average displacement. Changes in thermal population will change the average displacement in the ground state, and vertical excitation to the excited state will occur to different displacements and different effective frequencies on the enthalpic surface of the excited state. This will alter the temperature dependence of the band maximum, and this additional temperature dependence should correspond to the entropic portion of λ . Anharmonic effects could account for the temperature dependence of E_{op} for the symmetrical complexes in eqs 2.4 and 2.5 where ΔG° must be rigorously zero. The effects of Morse and other anharmonic oscillators on optical bandshapes and electron-transfer

rates have been previously analyzed to a sufficient degree to show that additional temperature effects do arise from them.⁴⁴⁻⁴⁶ Extending these analyses to include a rigorous definition of entropy and to the development of a quantum definition of the reorganization free energy is required to verify this hypothesis.

A common criticism of the application of a quantum mechanical model to electron-transfer reactions is the "assumption" that the solvent modes can be represented adequately as harmonic oscillators. It has long been argued that this assumption should not be made, but there is little quantitative evidence about how well or poorly either individual solvent librational modes or the collective solvation energy can be represented by a simple harmonic model. There are two issues. The first is whether it is appropriate to use a general quantized treatment for some or all of the solvent motions. The second is whether the quantized treatment needs to be harmonic or anharmonic in nature.

With regard to whether or not using a quantized treatment is required, we note the following. For the case of strongly hydrogen-bonding solvents such as water, the energy of interaction between two solvent molecules can easily be 6 kcal/mol (2100 cm⁻¹) with the frequency of the intermolecular modes being several hundred cm⁻¹.⁴⁷ Experimentally determined reorganizational energies for complexes of the type [Ru(NH₃)₅(L)]^{3+/2+} (L = pyridine, ...) in strongly hydrogen-bonding solvents have been found to be ~120 cm⁻¹ per solvent molecule.⁴⁸ Even for weakly polar and weakly hydrogen-bonding solvents such as benzene, the interactions between solvent molecules are ~2 kcal/mol (700 cm⁻¹).⁴⁹ For the strongest of these interactions, a quantized approach would not only be valid but required. For the weaker of these interactions, a quantized approach may not be necessary but would be appropriate. Given the demonstration here of the merger between the quantum and classical treatments with regard to dependence on ΔG° , there is no apparent reason why the quantum treatment cannot be used at least for some aspects of solvent behavior. This is an important point since, as noted in the Introduction, there are many solvent effects, particularly for hydrogen-bonding solvents, which are not adequately explained by the dielectric continuum treatment. The quantum treatment represents a framework by which some of these deficiencies can be addressed.

With regard to the assumption of harmonic oscillators, for the strongest solvent interactions, the harmonic treatment could well be accurate at room temperature. For the weaker interactions, an accurate treatment of any specific mode would need to include anharmonic effects. The treatment of collective modes might require the same. Both reorganizational energies and frequencies for specific and collective solvent modes would be expected to be temperature dependent given the changes in density and dielectric constant that occur with temperature and the likely strong anharmonic nature of the solvent librations. It might be possible to include these effects into a harmonic treatment by allowing both frequencies and reorganizational energies to be temperature dependent and by describing them phenomenologically. It would be more desirable to incorporate specific anharmonic models which would allow more physically based interpretations of experimental data.

We feel that the quantum treatment with harmonic oscillators and the incorporation of frequency changes is not an unreasonable model for nondynamical solvent behavior and at least qualitative features can be analyzed within that framework. The inclusion of anharmonicities would greatly increase the quantitative nature of this description and is being pursued. The fundamental relationships discussed here between optical and thermal electron transfer for a general quantum mechanical treatment, shown in eqs 3.20 and 3.21, do not rely directly on the assumption of the harmonic oscillator model. It relies, instead, on the validity of the method of moments put forth by Kubo⁷ and Lax³³ and the assumption that the third moment is small (i.e., the classical limit with small entropic changes). The harmonic oscillator model was invoked to demonstrate the range of applicability and to translate the moment expressions into thermodynamic or spectroscopic quantities. Thus, the solvent can be reasonably treated within

this scheme simply by its phenomenological effect on the band moments.

As was made apparent by the harmonic treatment, neglect of the third moment is a stringently limiting assumption and higher level expressions must be utilized even to include general entropic effects. We find the assumption of "classical" Gaussian band-shapes to be more restrictive than the assumption of harmonic potential functions. The inclusion of anharmonic effects will accentuate this distinction. Overall, this framework seems to provide an adequate forum within which the effects of such nonideal behavior could be studied, although quantitative information describing these perturbations is currently lacking. From current activity in the areas of developing more accurate potential functions for solvents and of improved molecular dynamics simulations, more accurate information on this type of behavior should be forthcoming.

Conclusions

1. We have measured the temperature dependence of the intervalence transfer band maximum (E_{op}) for an asymmetrical ligand-bridged complex where ΔG° has a substantial temperature dependence and shown that the two have very similar values. This demonstrates that E_{op} depends on ΔG° rather than ΔH° even for an optical transition where the dielectric continuum model is probably not appropriate.

2. We have developed a quantum mechanical, harmonic oscillator model for optical and thermal electron transfer which incorporates frequency changes, a feature which is necessary for $\Delta G^\circ \neq \Delta H^\circ$. In the classical limit with small frequency changes, it was shown that both the optical and thermal electron-transfer processes should depend on ΔG° rather than ΔH° in agreement with the classical, free-energy surface approach.

3. We have been unable to derive simple thermodynamic expressions for the optical and thermal processes of a truly asymmetrical system except in the limit of small frequency changes, which requires small entropic changes. Therefore, we feel that entropic effects are not included completely in the simple formulations which correspond to those derived classically. In other limits the optical and thermal processes are still rather simply related to one another.

4. The remaining distinction between the quantum mechanical and free energy surface descriptions of electron transfer is the distinction between enthalpic and free reorganization energies. In the quantum treatment, this distinction appears to be lost in the assumption of temperature independent, harmonic potential surfaces and will be resolved by the relaxation of that constraint.

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