

Estimation of Electron Transfer Rate Constant from Static (Optical and Thermodynamic) Measurements: A Study of $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+} + \text{Fe}(\text{CN})_6^{3-} \rightleftharpoons \text{Ru}(\text{NH}_3)_5\text{pz}^{3+} + \text{Fe}(\text{CN})_6^{4-}$ Electron Transfer Reactions

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A kinetic study of the electron-transfer reactions $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+} + \text{Fe}(\text{CN})_6^{3-} \rightleftharpoons \text{Ru}(\text{NH}_3)_5\text{pz}^{3+} + \text{Fe}(\text{CN})_6^{4-}$ was carried out in several water-organic solvent mixtures at 298.2 K. The free energies of activation for these thermal electron-transfer reactions were calculated from a combination of spectroscopic and thermodynamic data and are compared with those obtained from the kinetic study. Quantitative agreement is found between the two series of data. This shows the possibility of estimating activation free energies for electron-transfer reactions from these (static) measurements.

Introduction

The interest in relating electron-transfer reaction rates to spectroscopic measurements has been an area of growing interest as a consequence of the recent progress in understanding electron-transfer processes and the development of new spectroscopic techniques.¹ The studies in this field have to do mainly with electron transfer following optical excitation in contact radical ion pairs formed by excitation of charge-transfer complexes and nonradiative decay processes in metal to ligand excited states² and in vibronically excited binuclear complexes.³ However, studies in which optical electron transfers are related to the corresponding thermal electron transfer, when both the donor and the acceptor are in their ground state, are rather scarce and are of a qualitative character.^{4–6}

The connection between rate constants for electron-transfer processes and the corresponding optical spectra was derived several years ago by Hush,⁷ who obtained the equations for the reorganization energies, λ , and reaction free energies, ΔG° , from band energies, E_{op} , and widths, $\Delta\nu_{1/2}$, and for the electronic delocalization energies from the integrated band intensities. These relationships can be seen by considering the schematic

(monodimensional) representation of the free energy surfaces for an electron-transfer process depicted in Figure 1. If the response of the solvent is supposed to be linear, the free energy surfaces are parabolic. Indeed, it is frequently assumed, as Hush did, that the parabolas of the reactant and product states have the same curvature.⁸ In this simple approach, it follows (see Figure 1) that⁹

$$E_{\text{op}} = \lambda + \Delta G^\circ \quad (1)$$

and

$$\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda} = \frac{E_{\text{op}}^2}{4\lambda} \quad (2)$$

Equations 1 and 2 pointed to the possibility of using spectrally

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(9) There has been some controversy over using of the eq 1 because it is written in terms of energy (E_{op}) and free energy (ΔG° and λ). For this reason it was pointed out that on the right side of this equation, instead of λ and ΔG° , the corresponding energetic magnitudes should appear. Nevertheless, Marcus and Sutin have convincingly argued that parameters λ and ΔG° , appearing on the right-hand side of eq 1, are better viewed as free energies (see: Marcus, R. A.; Sutin, N. *Commun. Inorg. Chem.* **1986**, *5*, 119). It can also be argued that λ depends on the optical and static dielectric constants of the medium and ΔG° mainly on the static dielectric constant. As the temperature coefficients of these dielectric parameters are low, the entropic terms in λ and ΔG° must also be low and that they, indeed, compensate to some extent (see for example: Doong, Y.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 332). Finally, for an optical electron transfer, the nuclei are frozen, so the corresponding (electronic) entropy change would be

$$\Delta S = R \ln \frac{\Omega_{\text{exc}}}{\Omega_{\text{g}}}$$

where Ω is the spin multiplicity of the corresponding excited or ground state. Thus, the corresponding free energy term should be $\sim RT$, which is small in comparison to E_{op} and λ values. Consequently, λ and ΔG° can be taken as free energies. Indeed, in a dielectric continuum E_{op} and ΔG_{op} would be, strictly speaking, identical because a dielectric continuum assumes a harmonic bath and energies and free energies differences are the same for such a bath; the reaction field energies are also free energies of solvation (Bader, J. S.; Cortis, C. M.; Berne, B. J. *J. Chem. Phys.* **1997**, *106*, 2372).

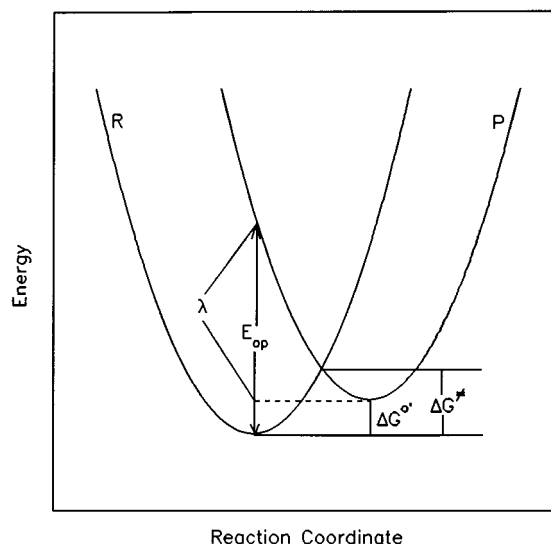


Figure 1. Free energy surfaces (FES) showing the characteristic magnitudes for the optical (vertical transition) and thermal (movement of representative point along the reaction coordinate) electron transfer.

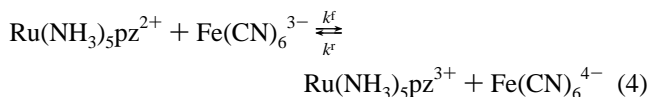
derived parameters to calculate the relevant parameters for thermal electron transfer. Thus, E_{op} can be measured directly and λ can be obtained from the full-width at half-height of the band, $\Delta\nu_{1/2}$, through⁷

$$\lambda \text{ (cm}^{-1}\text{)} = \frac{(\Delta\nu_{1/2})^2}{2295} \quad (\text{at } 298.2 \text{ K}) \quad (3)$$

in such a way that the activation free energy for the (thermal) electron-transfer process can be obtained from eq 2.

However, this approach is precluded from a practical point of view because of the phenomena of inhomogeneous broadening.^{5,10–12} An alternative approach, used in this work, is to employ a combination of spectroscopic and thermodynamic measurements. This consists of determining the value of E_{op} from the band and the reaction free energy from thermodynamic measurements.

In this paper, following this approach, we have studied the kinetics of the thermal electron-transfer processes



as well as the corresponding optical processes. The equilibrium constants for the reaction as in different media were also obtained. So, it was possible to compare the activation free energies obtained from optical (and thermodynamic) measurements with those directly obtained from kinetic data.

This comparison is of interest from different points of view: First, it permits a check on the (real) possibility of obtaining electron-transfer rate constants from static (optical and thermodynamic) measurements. This possibility is interesting by itself. Indeed, if ΔG^\ddagger can be obtained from these measurements, this opens the door to the *experimental* (near-direct) estimation of the preexponential term in the rate constants, as pointed out by Weaver et al.¹³ and Bu et al.¹⁴ This term, as is well-known,

contains information on the electronic and dynamical solvent effects on the electron-transfer reactions.

From another point of view, studies as the one presented in this paper permit the testing of implicit approximations in the Marcus–Hush model, viz., the idea that the free energy surfaces for the reactant and product states are (or can be taken as) parabolas of the same curvature.

Experimental Section

Materials. The complexes $[\text{Ru}(\text{NH}_3)_5\text{pz}](\text{ClO}_4)_2$ (pz = pyrazine) and $[\text{Ru}(\text{NH}_3)_5\text{py}](\text{ClO}_4)_2$ (py = pyridine) were prepared and purified according to the procedures described in the literature.^{15,16} The other reagents were all Anal. R. grade and used as purchased. The water used in the preparation of solutions had a conductivity $\sim 10^{-6} \text{ S m}^{-1}$.

Spectra. The spectra corresponding to the MMCT bands within the ion-pair $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}/\text{Fe}(\text{CN})_6^{4-}$ were obtained with a Hitachi U-2000 UV–visible spectrophotometer at 298.2 K.

The solutions containing this ion pair were prepared by mixing equal volumes of ruthenium(II) complex and hexacyanoferrate(III) solutions. The concentrations of the complexes were always 3×10^{-3} and $6 \times 10^{-3} \text{ mol dm}^{-3}$, respectively. An excess of pyridine ($[\text{py}] = 0.2 \text{ mol dm}^{-3}$) was added to the reactant solutions in order to avoid the formation of cyano-bridged species.¹⁷

Electrochemical Measurements. The redox potentials of $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_5\text{py}^{3+/2+}$ in water, in the presence of 0.3 mol dm^{-3} NaClO_4 , were obtained by cyclic voltammetry, using the apparatus, electrodes, and procedure previously described.¹⁸ In these measurements, a solution of the reduced component of the couple at $10^{-3} \text{ mol dm}^{-3}$ concentration was employed. The estimated uncertainty in the measured potentials is about 3 mV.

Equilibrium Measurements. The equilibrium constants, Q , for reaction 4 were measured by a spectrophotometric technique. These equilibrium constants were obtained from two different procedures. The first one consisting of mixing equal volumes of a solution containing $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$, at $1.04 \times 10^{-4} \text{ mol dm}^{-3}$ concentration (a_0), with another containing both $\text{Fe}(\text{CN})_6^{4-}$, at $3.8 \times 10^{-4} \text{ mol dm}^{-3}$ concentration (d_0), and $\text{Fe}(\text{CN})_6^{3-}$, at a concentration (b_0) ranging from 10^{-2} to $3.2 \times 10^{-2} \text{ mol dm}^{-3}$ (depending on the solvent). These concentrations were selected after preliminary experiments in order to produce a maximum change in the absorbance of the solutions.

In the second procedure, the concentrations of iron complexes in the first solution were the same as in the first case. The second solution contained both, $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$ at concentration, a_0 , $1.72 \times 10^{-5} \text{ mol dm}^{-3}$ and $\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}$ at concentration, c_0 , $8.8 \times 10^{-5} \text{ mol dm}^{-3}$ (the latter ruthenium complex was produced in situ by partial oxidation of ruthenium(II) complex by $\text{S}_2\text{O}_8^{2-}$ ¹⁹). All the solutions contained NaClO_4 at 0.3 mol dm^{-3} concentration.

Measurements were performed at 472 nm, corresponding to the maximum of the absorption spectrum of $\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}$. The values of Q were calculated from the measured absorbances at equilibrium, A_{eq} , according to equations

$$Q_{\text{I}} = \frac{[A_0 - A_{eq}][A_0 - A_{eq} + (\epsilon_1 + \epsilon_2)d_0]}{[A_0 - A_{eq} - (\epsilon_1 + \epsilon_2)a_0][A_0 - A_{eq} - (\epsilon_1 + \epsilon_2)b_0]} \quad (5a)$$

$$Q_{\text{II}} = \frac{[A_0 - A_{eq} - (\epsilon_1 + \epsilon_2)c_0][A_0 - A_{eq} - (\epsilon_1 + \epsilon_2)d_0]}{[A_0 - A_{eq} + (\epsilon_1 + \epsilon_2)a_0][A_0 - A_{eq} + (\epsilon_1 + \epsilon_2)b_0]} \quad (5b)$$

the first one corresponding to procedure I and the second to procedure II, where A_0 is the initial absorbance of the solutions, and ϵ_1 and ϵ_2

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Table 1. Energy Corresponding to the Maximum of the Absorption Spectra of the MMCT Band within the Ion Pair Ru(NH₃)₅pz²⁺/Fe(CN)₆⁴⁻ at 298.2 K in Several Aqueous Mixtures

% W ^a	D _s	E _{op} /kJ mol ⁻¹ ^b
Water/Ethylene Glycol		
0.0	78.5	108
10.0	75.6	106
20.0	72.8	105
Water/Methanol		
10.0	74.0	108
Water/Glucose		
6.4	77.2	109
13.1	75.4	111
Water/Acetonitrile		
10.0	74.7	107

^a % weight of organic cosolvent. ^b Obtained from the experimental values of E_{op} for the ion pair Ru(NH₃)₅py³⁺/Fe(CN)₆⁴⁻ by the equation (E_{op})_{pz} - (E_{op})_{py} = E_{py}^o - E_{pz}^o (assuming that the reorganization energies are the same for both ion pairs). E_{py}^o and E_{pz}^o are the standard formal redox potentials of the couples Ru(NH₃)₅py^{3+/2+} and Ru(NH₃)₅pz^{3+/2+} (0.322 and 0.517 V in water, respectively). The difference E_{py}^o - E_{pz}^o was measured, resulting in independence of the reaction media. Moreover, (E_{op})_{pz} was corrected from the spin-orbit coupling contribution using a λ_{so} value of 4.9 kJ mol⁻¹.^{17,23}

represent the molar absorption coefficient of the complexes Ru(NH₃)₅pz²⁺ and Fe(CN)₆³⁻ at λ = 472 nm, respectively.²⁰

Kinetic Measurements. Kinetics of the reactions in eq 4 were studied by the temperature-jump technique using a Hi-Tech Model SF-61 apparatus previously described.²¹ The concentrations of the solutions of Ru(NH₃)₅pz²⁺ and Fe(CN)₆³⁻ were 5 × 10⁻⁵ and 2 × 10⁻⁴ mol dm⁻³, respectively (both of them containing NaClO₄ at 0.3 mol dm⁻³ concentration). After both solutions were mixed, the absorbance was recorded up to equilibrium (at 298.2 K) at 472 nm. Under our working conditions, relaxation time is given by²²

$$\frac{1}{\tau} = k^f \{ Q([\text{Ru}(\text{NH}_3)_5\text{pz}^{2+}]_{\text{eq}} + [\text{Fe}(\text{CN})_6^{3-}]_{\text{eq}}) + [\text{Ru}(\text{NH}_3)_5\text{pz}^{3+}]_{\text{eq}} + [\text{Fe}(\text{CN})_6^{4-}]_{\text{eq}} \} \quad (6)$$

From this equation and from the values of Q = k^f/k^r, both rate constants can be obtained easily.

All the experimental results were obtained in buffered solutions pH = 5 ([AcO⁻] = [AcOH] = 5 × 10⁻³ mol dm⁻³).

Results

Table 1 gives the energies corresponding to the maxima of absorption spectra of the MMCT band within the ion pair Ru(NH₃)₅pz^{3+/2+}/Fe(CN)₆⁴⁻. Because of instrumental difficulties, we obtained the band corresponding to the ion pair Ru(NH₃)₅py^{3+/2+}/Fe(CN)₆⁴⁻ instead of that of the Ru(NH₃)₅pz^{3+/2+}/Fe(CN)₆⁴⁻ ion pair. From this band it is a straightforward matter to obtain E_{op} for the ion pair of interest using the standard formal redox potentials of the couples Ru(NH₃)₅py^{3+/2+} and Ru(NH₃)₅pz^{3+/2+} and the spin-orbit coupling contribution^{17,23} (see details in Table 1).

Table 2 contains the values of the constants for the equilibrium in eq 4, Q. The relaxation times for this system are also

Table 2. Equilibrium Constants, Q, Relaxation Times, τ, and the Rate Constants for the Forward, k^f, and the Reverse, k^r, Processes for the Reaction (Eq 4) at 298.2 K

% W ^a	10 ² Q ^b	τ/μs	10 ⁻⁷ k ^f /M ⁻¹ s ⁻¹	10 ⁻⁹ k ^r /M ⁻¹ s ⁻¹
Water/Ethylene Glycol				
0.0	5.3	22	10.3	1.94
10.0	3.1	21	8.31	2.68
20.0	1.8	27	4.94	2.75
Water/Methanol				
10.0	1.8	30	4.45	2.47
Water/Glucose				
6.4	5.2	20	11.2	2.16
13.1	5.4	25	9.16	1.70
Water/Acetonitrile				
10.0	1.3	34	3.34	2.57

^a % weight of organic cosolvent. ^b Q values are the average of equilibrium constants obtained from the two procedures mentioned in the text. The uncertainty between the two sets of values was ca. 5%.

included in the table, as well as the values of k^f and k^r obtained as previously described.

Discussion

To use eq 2, the free energy for the thermal electron-transfer processes, ΔG^{o'}, must be obtained from the data of equilibrium, after correction of the work terms,²⁴ through

$$\Delta G^{\circ} = -RT \ln Q \quad (7)$$

and

$$\Delta G^{\circ'} = \Delta G^{\circ} + w_p - w_r \quad (8)$$

w_r in eq 8 represents the work corresponding to the precursor complex formation from the separate reactants, and w_p is the equivalent for the formation of the successor complex from the separate products. These work terms were obtained using the Eigen-Fuoss treatment.²⁵ In calculation of the work terms, a critical parameter is the distance of closest approach in the ion pair (the precursor complex). This distance depends on the side by which the ruthenium complex approaches the iron complex. Given that there is some controversy involved,^{17,22,23} we have performed calculations corresponding to two possibilities, that is, the approach from the ammonia or the pyrazine side. Better results corresponded to the latter, in agreement with Haim's suggestion.²² The values of ΔG^{o'} are given in Table 3.

From the data of ΔG^{o'} and E_{op} the values of the free energies of reorganization and activation were obtained, using eqs 1 and 2, respectively, the latter modified in order to include the influence of the coupling energy, H_{ab}.²⁶

$$\Delta G^{\ddagger} = \frac{E_{\text{op}}^2}{4\lambda} - H_{\text{ab}} \quad (9a)$$

$$H_{\text{ab}} = \frac{2.05 \times 10^{-2}}{r} (\epsilon_{\text{max}} \nu_{\text{max}} \Delta \nu_{1/2})^{1/2} \quad (9b)$$

where ε_{max} is the molar absorption coefficient at the band maximum and r is the distance separating the redox sites in Å.

- (20) The molar absorption coefficients of the complexes Ru(NH₃)₅pz²⁺ and Fe(CN)₆³⁻ are ε₁ = 12 956 mol⁻¹ dm³ cm⁻¹ and ε₂ = 14 mol⁻¹ dm³ cm⁻¹, respectively, at 472 nm in the presence of 0.3 mol dm⁻³ NaClO₄.
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Table 3. Free Energy Change, ΔG° , Reorganization Energy, λ , and Free Energy of Activation, $(\Delta G^\ddagger)_{\text{op}}$, for the Forward ($i = f$) and the Reverse ($i = r$) Electron-Transfer Processes at 298.2 K Obtained from Thermodynamic and Optical Data

% W ^a	$\Delta G^\circ /$ kJ mol ^{-1 b}	$\lambda /$ kJ mol ^{-1 c}	$(\Delta G^\ddagger)_{\text{op}} /$ kJ mol ⁻¹	$(\Delta G^\ddagger)_{\text{op}} /$ kJ mol ⁻¹
Water/Ethylene Glycol				
0.0	-2.7	111.0	28.5	25.8
10.0	-3.9	111.2	29.2	24.8
20.0	-5.1	110.4	29.6	24.5
Water/Methanol				
10.0	-5.2	113.5	30.4	25.2
Water/Glucose				
6.4	-2.6	111.9	28.7	26.0
13.1	-2.5	113.8	29.1	26.6
Water/Acetonitrile				
10.0	-6.1	113.4	30.8	24.8

^a % weight of organic cosolvent. ^b $\Delta G^\circ = -\Delta G_r^\circ$ ^c $\lambda_f = \lambda_r$.

Table 4. Formation Constant of the Ion Pair, K_{os}^i , True Electron-Transfer Rate Constant, k_{et}^i , and Free Energy of Activation, $(\Delta G^\ddagger)_{\text{th}}$, for the Forward ($i = f$) and the Reverse ($i = r$) Electron-Transfer Processes Obtained from Kinetic Data at 298.2 K

% W ^a	$K_{\text{os}}^f /$ M ⁻¹	$K_{\text{os}}^r /$ M ⁻¹	$10^{-7}k_{\text{et}}^f /$ s ⁻¹	$10^{-7}k_{\text{et}}^r /$ s ⁻¹	$(\Delta G^\ddagger)_{\text{th}} /$ kJ mol ⁻¹	$(\Delta G^\ddagger)_{\text{th}} /$ kJ mol ⁻¹
Water/Ethylene Glycol						
0.0	6.5	41.7	1.59	4.65	27.4	24.7
10.0	6.6	44.2	1.25	6.07	28.0	24.1
20.0	6.8	46.8	0.72	5.88	29.4	24.2
Water/Methanol						
10.0	6.7	45.6	0.66	5.42	29.6	24.3
Water/Glucose						
6.4	6.5	42.8	1.71	5.05	27.2	24.5
13.1	6.7	44.4	1.37	3.83	27.8	25.2
Water/Acetonitrile						
10.0	6.7	45.0	0.50	5.71	30.3	24.2

^a % weight of organic cosolvent.

It is worth pointing out that H_{ab} was calculated for the ion pair Ru(NH₃)₅py³⁺/Fe(CN)₆⁴⁻. It was assumed that the value of this parameter for the electron transfer within the ion pair Ru(NH₃)₅pz³⁺/Fe(CN)₆⁴⁻ is the same. The value of H_{ab} in pure water is $70 \text{ cm}^{-1} = 0.84 \text{ kJ mol}^{-1}$ ($\epsilon_{\text{max}} = 33 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ and $\Delta\nu_{1/2} = 4614 \text{ cm}^{-1}$). The value of H_{ab} in other solvents is the same as that in water because neither ϵ_{max} nor $\Delta\nu_{1/2}$ showed significant modifications in the medium. To calculate the free energy of activation by eq 9a, a value of H_{ab} was used, which is ca. 75% of the H_{ab} value obtained from the MMCT. This difference arises because the optical and thermal electron transfers occur at different points along the reaction coordinate.²⁷ The results of these calculations appear in Table 3 as, λ and $\Delta G_{\text{op}}^\ddagger$.

Now the activation free energy will be obtained from kinetic data. In this regard, obviously, the data appearing in Table 2 cannot be used directly, since the activation free energies obtained from the data corresponding to the optical electron transfer are those of the true electron-transfer rate constants, k_{et} . These rate constants are related to k^f (or k^r) through

$$k^i = K_{\text{os}}^i k_{\text{et}}^i \quad (i = f, r) \quad (10)$$

K_{os}^i being the association constant corresponding to the formation of the ion pairs from the separate reactants or products.

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Thus, the k_{et} values must be obtained. These values, appearing in Table 4, were found by division of k^i by K_{os}^i , the latter being calculated as in ref 22.

From the k_{et} values, the free energies of activation were obtained using the semiclassical equation:²⁴

$$k_{\text{et}} = \kappa_{\text{el}} \nu_{\text{n}} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (11)$$

Here κ_{el} , ν_{n} and ΔG^\ddagger are the electronic transmission coefficient, the nuclear frequency factor, and the activation free energy, respectively.

A value of $\kappa_{\text{el}} \sim 0.2$ can be calculated from H_{ab} using²⁸

$$\kappa_{\text{el}} = \frac{2P}{1+P} \quad (12)$$

$$P = 1 - \exp\left[-\frac{H_{\text{ab}}^2}{h\nu_{\text{n}}}\left(\frac{4\pi^3}{k_{\text{B}}T\lambda}\right)^{1/2}\right] \quad (13)$$

As to the nuclear frequency factor, ν_{n} , eq 14 was employed in order to obtain it:²⁹

$$\nu_{\text{n}} = \left[\frac{\nu_{\text{in}}^2 \lambda_{\text{in}} + \nu_{\text{out}}^2 \lambda_{\text{out}}}{\lambda_{\text{in}} + \lambda_{\text{out}}}\right]^{1/2} \quad (14)$$

In this equation ν_{in} and ν_{out} are the characteristic frequencies for internal and external (solvent) reorganizations, and λ_{in} and λ_{out} , the corresponding contributions to λ .

Calculations with this equation and the corresponding parameters appearing in it^{23,29-33} gave the values of ν_{n} . From ν_{n} and κ_{el} we have obtained values of the preexponential factor ranging from 0.9×10^{12} to $1.13 \times 10^{12} \text{ s}^{-1}$. Consequently, (according to the suggestion of one of the referees) we used an average value of $1 \times 10^{12} \text{ s}^{-1}$ for this parameter. Using this value, the free energies of activation corresponding to thermal electron-transfer reactions were found. These values are given in Table 4 as $\Delta G_{\text{th}}^\ddagger$.

A comparison of activation free energies in Tables 3 (optical) and 4 (thermal) shows excellent agreement between both sets of data. So, the possibility of using the developed approach to estimate ΔG^\ddagger seems adequate.

It is worth pointing out that the agreement between kinetic and calculated free energies of activation is found in the case of both the forward and reverse electron-transfer processes. Taking into account that calculations were performed by using the same value of λ for both processes, the results obtained in this work show that the approximation of taking the free energy surfaces for the reactant and product states as parabola of the same curvature is good enough. On the other hand, the value of λ was calculated from optical (and thermodynamic) data. This implies that part of the free energy curve corresponding to high energy (that is, to a high value of reaction coordinate) is

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involved. Consequently, the agreement between optical and thermal free energy of reaction implies that the parabolic character of the free energy of activation is maintained (at least as a good approximation) at these high values of the reaction coordinate, implying that the response of the solvent is linear in a good approximation. In fact, this result is in agreement with those of Warshel³⁴ and others^{35,36} obtained from simulation of electron-transfer processes.

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