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The solvent effect on electronic energy transfer between excited $[Ru(bpy)_3]^{2+}$ donor and aromatic acceptors

Idalina M.M. de Carvalho, Marcelo H. Gehlen*

Instituto de Química de São Carlos – Universidade de São Paulo, Caixa Postal 780, CEP 13560-970, São Carlos-SP, Brazil

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Abstract

The luminescence quenching of $[Ru(bpy)_3]^{2+}$ by a series of organic aromatic molecules in acetonitrile occurs by electronic energy transfer through exchange interaction, and the quenching rate constants obtained are below the diffusion-controlled limit. The measured free energy of activation for energy transfer between non-highly distorted excited states is ascribed, in part, to a solvation effect due to the dipolar nature of MLCT excited-state of the $[Ru(bpy)_3]^{2+}$ donor. The solvent reorganization energy, obtained from quenching data, is 5.5 ± 0.5 kcal/mol, in agreement with the predicted value of 5.7 kcal/mol, assuming the electronic transition $(d\pi)^5(L\pi)^1 \rightarrow (d\pi)^6$ is the Ru complex as an internal electron transfer mediated by solvent reorganization, calculated using the one-sphere model for charge redistribution. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Electronic energy transfer; Solvent effect; Ru complex; Luminescence quenching

1. Introduction

The kinetics of energy transfer via exchange interaction was described by Dexter [1], and the dependence of the rate constant in a bimolecular process with the energy difference between donor and acceptor electronic levels was first elaborated by Sandros [2,3], and later modified by Balzani et al. [4,5] using the classical treatment of transition-state theory in electron-transfer processes. Several experimental systems, including the quenching of aromatic triplets by *cis* and *trans*-stilbene [6,7], by metallocenes [8–11], and by metal β-diketonate complexes [12–14], which did not follow the behavior predicted by the Sandros equation, were explained by the Balzani treatment [5]. The role of the reorganization energy, mainly due to nuclear rearrangements of reactants, was established as an important contribution to the intrinsic energy barrier of the electronic-energy transfer process.

Energy-transfer rates in solution for coordination compounds are usually lower than the diffusion controlled limit, being influenced by the charge, the geometry and the ligand size of the complexes [15–19]. Moreover, bimolecular exchange energy transfer in constrained media, particularly in micelles [20–22], cyclodextrins [23], and other cage-type molecules [24,25] have been also investigated, and a different kinetics behavior compared to homogeneous solvent reaction has been verified. More recently, solvent inhomogeneity and clustering effects in supercritical fluids have been investigated using triplet–triplet energy transfer between aromatic probes [26].

It is recognized that photoinduced triplet–triplet energy transfer is an interesting tool for studying the effect of electronic coupling between frontier orbitals of donor and acceptor molecules, specially in model compounds [27–33]. Energy transfer in the Marcus inverted region has been experimentally determined in donor–acceptor systems through unimolecular [34,35] and bimolecular [36,37] reactions.

A common trend in energy transfer between neutral molecules is that the rate of the process is little affected by solvent reorganization, in contrast with the electron transfer which is largely a solvent-dependent process. However, when the reaction involves ions or when the ground and excited dipole moments of donor or acceptor are substantially different, reorganization of solvent dipoles along the reaction path may be part of the intrinsic barrier of the electronic energy-transfer process.

The evidence of electronic energy transfer between the $[Ru(bpy)_3]^{2+}$ and organic acceptors was first reported by Wrighton and Markham [38] in the ethanol : benzene

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*Corresponding author. Tel.: +55-16-274-9208; fax: +55-16-273-9205; e-mail: marcelog@iqsc.sc.usp.br

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solvent system. In our work, the luminescence quenching of the MLCT excited state of the $[Ru(bpy)_3]^{2+}$ by a series of aromatic compounds in an acetonitrile solution is analyzed with focus on the solvent reorganization effect, and using the framework of the semi-classical Marcus theory of electron transfer.

2. Experimental

The luminescence probe 2,2′-bipyridine ruthenium (II) dichloride, $[Ru(bpy)_3]^{2+}$, was purchased from Smith Chemical, and used as received. The aromatic compounds were recrystallized in appropriated solvents when required, or used directly when of scintillation degree.

Corrected steady-state luminescence spectra of the $[Ru(bpy)_3]^{2+}$ complex (5×10^{-5} M) were recorded on a CD-900 Edinburgh spectrofluorimeter, and the intensity was calculated from integration of the emission band. The luminescence lifetime of the complex in acetonitrile was obtained from the time-resolved single-photon counting technique using the CD-900 Edinburgh spectrometer operating with a hydrogen-filled nanosecond flash lamp. All luminescence measurements were taken with the samples thermalized, in air-equilibrated conditions at 298 K, and with excitation in the maximum of the MLCT absorption band of the Ru complex. The triplet energy of the aromatic compounds were determined from the crossing point between the normalized excitation and emission phosphorescence spectra at 77 K in 1 : 1 acetonitrile/1-iodopropane solution.

3. Results and discussion

Luminescence quenching of$[Ru(bpy)_3]^{2+}$ MLCT excited-state in acetonitrile is observed after the addition of aromatic compounds, such as anthracene and pyrene derivatives. The relative luminescence intensity follows a linear Stern–Volmer relation (see Fig. 1). The slope of the plots is the Stern–Volmer constant, $K_{sv} = k_q \tau_0$, where k_q is the second-order luminescence quenching rate constant and τ_0 the luminescence lifetime of the probe in an aerated solution. Using the experimentally determined luminescence probe lifetime of 180 ± 2 ns, the K_{SV} values for a series of aromatic quenchers were converted into the respective quenching rate constants. The values obtained are given in Table 1 and listed with the triplet energy of the quenchers. The triplet energy determined is close to the previous values cited in the literature [39,40].

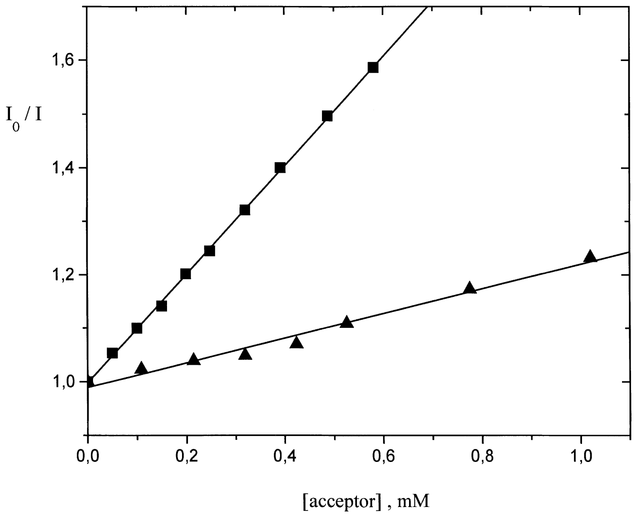


Fig. 1. Stern–Volmer plots of the luminescence quenching of $[Ru(bpy)_3]^{2+}$ by anthracene (■), and pyrene (▲), in acetonitrile at 298 K.

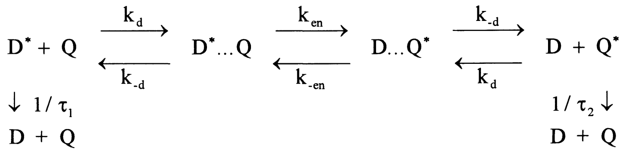
The decrease of k_q with the energy difference between of electronic excited triplet state of the Ru complex and aromatic quenchers indicates that a possible mechanism of quenching involves electronic energy transfer. The possibility of electron transfer is ruled out, since the free-energy change is positive when the redox potentials of the reactants are taken into consideration. Furthermore, the triplet–triplet energy transfer is confirmed from the observation of sensi-

Table 1
Luminescence quenching rate constants of the MLCT excited-state of $[Ru(bpy)_3]^{2+}$ by organic aromatic acceptors in acetonitrile at 298 K

Quencher	$k_q/(10^9\ M^{-1}\ s^{-1})$	E_{0-0}/(kcal/mol) [a]	E_{0-0}(kcal/mol) [b] (solvent, Ref. No.)
1,6-Diphenyll,3,5 hexatriene	5.6 ± 0.3	35.8	35.4 (*n*, 2)
9-Carboxianthracene	6.3 ± 0.3	36.7	
9,10-Dibromoanthracene	5.8 ± 0.4	40.2	40.1 (*n*, 2)
9-Methylanthracene	5.9 ± 0.3	39.8	41.1 (*n*, 2)
9,10-Diphenylanthracene	5.2 ± 0.4	41.5	41.8 (*n*, 1)
Anthracene	5.7 ± 0.2	42.8	42.7 (*p*, 1)
1-Pyrenecarboxaldehyde	4.5 ± 0.2	44.5	44.4 (*n*, 2)
Acridine	3.8 ± 0.2	45.9	45.1 (*n*, 2)
9-Aminoacridine	2.8 ± 0.2	46.3	45.8 (*p*, 3)
Pyrene	1.3 ± 0.1	48.1	48.2 (*p*, 1)
trans-Stilbene	0.4 ± 0.1	49.5	50.0 (*n*, 1)

[a] The E_{0-0} triplet energy of $[Ru(bpy)_3]^{2+}$ MLCT excited-state is 49 kcal/mol.(p,2) Experimental values obtained here.

[b] Values reported in the literature; *n*, non-polar solvent; *p*, polar solvent. (1), Ref. [39]; (2), Ref. [40]; and (3), Ref. [41].



Scheme 1.

tized phosphorescence at 77 K of some of the pairs investigated.

Application of the Sandros equation [2,3] to the k_q and ΔE_{00} data does not yield satisfactory fitting result. The shortcoming lies in that the quenching rate constants measured are smaller than the values predicted by the Sandros equation, which points to the presence of a certain intrinsic barrier in the energy-transfer process. This result demands the use of a more elaborate kinetics in which the quenching mechanism may be written as [4,5] (Scheme 1).

In the steady-state approximation, and assuming that $1/\tau_2 \gg k_d[D]$, the experimental quenching rate constant k_q is given by

$$k_q = k_d\left(1 + K^{-1} + \frac{k_{-d}}{k_{en}}\right)^{-1} \quad (1)$$

where $K = k_{en}/k_{-en}$, is the ratio of the forward and backward energy-transfer rate constants, and k_d and k_{-d} the association and dissociation diffusion rate constants of the donor–acceptor pair, respectively. Eq. (1) can be written in terms of free activation energy of the forward energy transfer step, $\Delta G^{\#}$, and the standard free energy of reaction, ΔG^0,

$$k_q = k_d\left(1 + e^{\Delta G^0/RT} + (k_{-d}/\nu^0_{en})e^{\Delta G^{\neq}/RT}\right)^{-1} \quad (2)$$

The free-energy change has been estimated from the difference between the triplet electronic energy of the donor and acceptor. When entropy difference between ground and excited states is very small, the driving force is approximately given by [42]

$$\Delta G^0 \approx -E_{0-0}(D^*, D) + E_{0-0}(Q^*, Q) \quad (3)$$

The plot of the experimental quenching rate constant k_q as a function of ΔG^0 is shown in Fig. 2. The free-energy change, ΔG^0, was calculated using Eq. (3), where $E_{0-0}(D^*,D)$ is taken as 49 kcal/mol [40], and $E_{0-0}(Q^*,Q)$ as the triplet energy value of the quenchers determined in this work.

In analogy with the theory used to describe the electron-transfer reactions, the experimental data were fitted to Eq. (2), considering the energy-transfer process in the non-adiabatic limit, where the frequency factor ν^0_{en} and $\Delta G^{\#}$ in the semi-classical approximation in the high-temperature limit are given by [43]

$$\nu^0_{en} = \frac{2\pi}{\hbar(4\pi\lambda RT)^{1/2}} H^2_{DA} \quad (4)$$

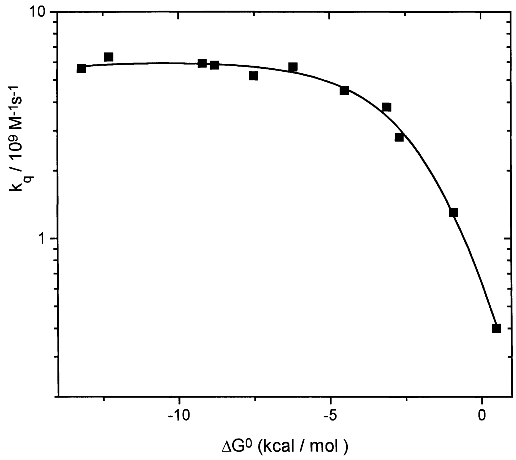


Fig. 2. Plot of the luminescence quenching rate constant k_q as a function of the free energy. Fitting using Eqs. (2)–(5) (see text for more details).

$$\Delta G^{\neq} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^0}{\lambda}\right)^2 \quad (5)$$

where H^2_{DA} is the squared electron-exchange matrix element, and λ the reorganization energy. The fitting result using Eq. (2) combined with Eqs. (3)–(5) was $\lambda = 10.5 \pm 0.5$ kcal/mol, $k_d = (6.5 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$, and $k_{-d}/\nu^0_{en} = 0.10 \pm 0.02$. In the earlier studies, an inverted region in electronic energy transfer was observed for driving forces of 9.0 kcal/mol [24], and 7.3 kcal/mol [35], depending of the system investigated. In the present case, the inverted region is not clearly observed in the plot of the quenching rate constant as a function of the driving force due to the diffusion effect in this bimolecular system. The rate constant of a diffusion controlled reaction considering spherical particles in acetonitrile is ca. (1–2) $\times 10^{10}\ M^{-1}\ s^{-1}$. The lower value obtained for k_d suggests that the quenching process has a kind of conformational or steric effect related to orbital overlap necessary for energy transfer. Using the Eigen–Fuoss equation [44,45], k_{-d} is estimated as $2 \times 10^9\ s^{-1}$. Using Eq. (4) and the observed value of $k_{-d}/\nu^0_{en} = 0.10$, the average degree of electronic coupling is calculated as $H_{DA} = 7 \pm 1\ cm^{-1}$. The magnitude of H_{DA} obtained here is of the same order as that determined in the study of bimolecular energy-transfer quenching of bipyridine complexes of Os(II) by anthracene (2.5 cm^{-1}) and 2,3-benzanthracene (8.5 cm^{-1}) [37].

The value obtained for the reorganization energy λ deserves a more elaborate analysis. Here, λ is the sum of the inner sphere (λ_{in}) and solvent (λ_s) reorganization energies. The inner contribution concerning bond rearrangement is predicted to be low for both, $[Ru(bpy)_3]^{2+}$ and aromatic acceptors used, since their electronic transitions do not involve very distorted states [5,46,47]; the former being of the order of 1300 cm^{-1}, and the latter between 300–700 cm^{-1}. Within these approximations, the average solvent reorganization energy λ_s is estimated at 5.5 ± 0.5 kcal/mol. This value is substantially high, considering an energy-transfer process where no liquid charge is commuted between reactants, but it is much lower than the outer-sphere reorganization energy calculated in a hypothetical situation of electron transfer in acetonitrile [48] (~19 kcal/mol, assuming donor and acceptor radii of 6 and 4 Å, respectively).

The MLCT excited state is considered to be a polar state because of localization of the promoted electron on a single bipyridine ligand [49]. This difference in charge distribution can lead to a change in solvation, and in a triplet–triplet energy-transfer process it may give rise to a solvent reorganization barrier. In order to evaluate this possibility, one can imagine the complex transition $(d\pi)^1(L\pi)^1 \rightarrow (d\pi)^6$ as an 'internal' electron-transfer process mediated by solvent reorganization. There is some free space between the planar rings of the bipyridine ligands in which the solvent can penetrate. This contribution can be estimated using the one-sphere model [50] for intramolecular electron-transfer process, when both the redox sites are embedded in a single spherical cavity (here, the boundaries of the Ru complex, defined hereinafter as R). Assuming that the internal dielectric constant D_{in} does not differ appreciably from the optical dielectric constant ($D_{\mathrm{in}} \cong D_{\mathrm{op}}$), and the angle between the vectors pointed from the center of the sphere to the redox sites is zero, the equation for the solvent reorganization energy is reduced to:

$$\lambda_{\mathrm{s}} = \frac{(\Delta e)^2}{R}\left(\frac{1}{D_{\mathrm{op}}} - \frac{1}{D_{\mathrm{s}}}\right)\sum_{n=1}^{\infty}\Phi_n \qquad (6)$$

and,

$$\Phi_n = \tfrac{1}{2}(\alpha^{2n} + \beta^{2n} - 2(\alpha\beta)^n)(1 + nD_{\mathrm{op}}/D_{\mathrm{s}}(n+1))^{-1} \qquad (7)$$

where $\alpha = r_{\mathrm{a}}/R$, and $\beta = r_{\mathrm{b}}/R$, with r_{a} and r_{b} as the Ru $d\pi$ radius and the average radius of the $L\pi^*$ of the bipyridine ligand in the molecular structure of the complex, respectively. Introducing the standard values of the optical ($D_{\mathrm{op}} = 1.801$) and solvent dielectric constant ($D_{\mathrm{s}} = 36.7$) for acetonitrile at 298 K in Eqs. (6) and (7), and assuming R=7 Å (Ru-to-bpy edge distance), r_{a}=1.3 Å (covalent radius of Ru(III), and $r_{\mathrm{b}} = 4.5$ Å, the solvent reorganization energy is estimated at 5.7 kcal/mol. Changes in the radii of ca. 0.5 Å give uncertainties of ± 2 kcal/mol in λ_{s}.

The MLCT absorption and emission bands of $[\mathrm{R(bpy)_3}]^{2+}$ show little solvent dependence [51]. However, the emission band has a strong blue shift when the complex is frozen in solid solvent matrix at temperatures below the glass transition of the solvent, whereas the absorption band in less susceptible to changes in solvent viscosity [52]. If the equilibrium solvent structure around the complex in the ground state is frozen at 77 K, then emission at low temperatures will occur from the complex in a similar solvent arrangement as that of the ground state. Thus, the difference in position and shape of the band envelop at 77 and 298 K may reflect, in part, the reorganization/coupling of the solvent molecules with the excited state in a fluid medium. The spectral shift between the emissions in frozen and liquid acetonitrile was measured and is ca. 1500 cm^{-1}, which corresponds to 4.3 kcal/mol. Note that this value is within the range of solvent reorganization energy measured by quenching data as well as that calculated using the one-sphere model.

In energy transfer, where non-highly distorted excited states are involved, the changes in the rate constants may result from modifications of the frequency or pre-exponential factor ν_{en}^0, on account of specific electronic coupling among different donor–acceptor pairs. However, this effect is more pronounced when metal-centered excited states are involved [13,53,54], this not being the present case.

4. Conclusions

The luminescence quenching of $[\mathrm{Ru(bpy)_3}]^{2+}$ by a series of organic aromatic molecules in acetonitrile occurs by electronic energy transfer and the quenching rate constants are below the diffusion controlled limit. The reorganization energy of 10.5 kcal/mol obtained from the fit of the quenching data can be ascribed, in part, to a solvation effect due to the dipolar nature of ^{3}MLCT excited-state of the $[\mathrm{Ru(bpy)_3}]^{2+}$ donor. The solvent reorganization energy calculated is 5.5 ± 0.5 kcal/mol, being close to the predicted value of 5.7 kcal/mol, estimated by the one-sphere model for charge redistribution.

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References

[1] D.L. Dexter, J. Chem. Phys. 21 (1953) 836.
[2] K. Sandros, Acta Chem. Scand. 18 (1964) 2355.
[3] K. Sandros, Acta Chem. Scand. 27 (1973) 3021.
[4] V. Balzani, F. Bolletta, J. Am. Chem. Soc. 100 (1978) 7404.
[5] V. Balzani, F. Bolletta, F. Scandola, J. Am. Chem. Soc. 102 (1980) 2152.
[6] W.G. Herkstroeter, G. Hammond, J. Am. Chem. Soc. 88 (1966) 4769.
[7] J. Saltiel, D.W.L. Chang, E.D. Megarity, A.D. Rousseau, P.T. Shannon, D. Thomas, A.K. Uriarte, Pure Appl. Chem. 41 (1975) 559.
[8] M. Kikuchi, K. Kikuchi, H. Kokubun, Bull. Chem. Soc. Jpn. 47 (1974) 1331.
[9] A. Farmilo, F. Wilkinson, Chem. Phys. Letts. 34 (1975) 575.
[10] W.G. Herkstroeter, J. Am. Chem. Soc. 97 (1975) 4161.
[11] A.P. Chapple, J.P. Vikesland, F. Wilkinson, Chem. Phys. Letts. 50 (1977) 81.
[12] F. Wilkinson, A. Farmilo, J. Chem. Soc. Faraday Trans. 2(72) (1976) 604.
[13] F. Wilkinson, C. Tsiamis, J. Chem. Soc. Faraday Trans. 2(77) (1981) 1681.
[14] S.Y. Huang, H.D. Gafney, J. Phys. Chem. 83 (1979) 1902.

[15] A. Adamczyk, F. Wilkinson, J. Chem. Soc. Faraday Trans. 2(68) (1972) 2031.
[16] F. Bolletta, M. Maestri, L. Moggi, V. Balzani, J. Am. Chem. Soc. 95 (1973) 7864.
[17] J.F. Endicott, M.J. Heeg, D.C. Gaswick, S.C. Pyke, J. Phys. Chem. 85 (1981) 1777.
[18] F. Wilkinson, C. Tsiamis, J. Phys. Chem. 85 (1981) 4153.
[19] S.E. Mazzetto, M.H. Gehlen, M.G. Neumann, D.W. Franco, J. Photochem. Photobiol. A: Chem. 104 (1997) 39.
[20] G. Rothenberger, P.P. Infelta, M. Grätzel, J. Phys. Chem. 83 (1979) 1871.
[21] R. Wang, Y. Liang, R.H. Schmehl, Inorg. Chim. Acta 225 (1994) 275.
[22] J.R. Darwent, W. Dong, C.D. Flint, N.W. Scharpe, J. Chem. Soc. Faraday Trans. 89 (1993) 873.
[23] A. Ponce, P.A. Wong, J.J. Way, D. Nocera, J. Phys. Chem. 97 (1993) 11137.
[24] A. Farrán, K.D. Deshayes, J. Phys. Chem. 100 (1996) 3305.
[25] A.J. Parola, F. Pina, E. Ferreira, M. Maestri, V. Balzani, J. Am. Chem. Soc. 118 (1996) 11610.
[26] D.R. Worrall, F. Wilkinson, J. Chem. Soc. Faraday Trans. 92 (1996) 1467.
[27] G.L. Closs, P. Piotrowiak, J.M. MacInnis, G.R. Fleming, J. Am. Chem. Soc. 110 (1988) 2652.
[28] J.F. Endicott, Acc. Chem. Res. 21 (1988) 59.
[29] G.L. Closs, M.D. Johnson, J.R. Miller, P. Piotrowiak, J. Am. Chem. Soc. 111 (1989) 3751.
[30] Y. Lei, T. Buranda, J.F. Endicott, J. Am. Chem. Soc. 112 (1990) 8820.
[31] H. Katayama, S. Ito, M. Yamamoto, J. Phys. Chem. 96 (1992) 10115.
[32] Y. Wang, K.S. Schanze, Chem. Phys. 176 (1993) 305.
[33] F. Barigelletti, L. Flamigni, J.P. Collin, J.P. Sauvage, Chem. Commun. (1997) 333.
[34] M.E. Sigman, G.L. Closs, J. Phys. Chem. 95 (1991) 5012.
[35] D.B. MacQueen, J.R. Eyler, K.S. Schanze, J. Am. Chem. Soc. 114 (1992) 1897.
[36] Z. Murtaza, A.P. Zipp, L.A. Worl, D. Graff, W.E. Jones Jr., W.D. Bates, T.J. Meyer, J. Am. Chem. Soc. 113 (1991) 5113.
[37] Z. Murtaza, A.P. Zipp, L.A. Worl, D. Graff, W.E. Jones Jr., W.D. Bates, T.J. Meyer, J. Phys. Chem. 98 (1994) 10504.
[38] M. Wrighton, J. Makham, J. Phys. Chem. 77 (1973) 3042.
[39] S.L. Murov, Handbook of Photochemistry, Marcel Dekker, New York, 1973.
[40] I. Carmichael, G.L. Hug, in: J.C. Scaiana (Ed.), Handbook of Organic Photochemistry, vol. I, Chap. 16, CRC Press, 1989.
[41] K. Kasama, K. Kikuchi, Y. Nishida, H. Kokubun, J. Phys. Chem. 85 (1981) 4148.
[42] The free energy difference includes the classical part of the reorganizational energy (see Ref. [37] for more details).
[43] R.A. Marcus, N. Sutin, Biochem. Biophys. Acta 811 (1985) 265.
[44] M. Eigen, Z. Phys. Chem. 1 (1954) 176.
[45] R.M. Fuoss, J. Am. Chem. Soc. 80 (1958) 5059.
[46] G.A. Crosby, W.G. Perkins, D.M. Klassen, J. Chem. Phys. 43 (1965) 1498.
[47] N. Sutin, C. Creutz, Pure Appl. Chem. 52 (1980) 2717.
[48] G.J. Kawarnos, Fundamentals of Photoinduced Electron Transfer, VCH publisher, New York, 1993, pp. 317.
[49] R.F. Dallinger, W.H. Woodruff, J. Am. Chem. Soc. 101 (1979) 4391.
[50] B.S. Brunschwig, S. Ehrenson, N. Sutin, J. Phys. Chem. 90 (1986) 3657.
[51] J.V. Caspar, T.J. Meyer, J. Am. Chem. Soc. 105 (1983) 5583.
[52] F. Barigelletti, P. Belser, A. von Zelewsky, A. Juris, V. Balzani, J. Phys. Chem. 89 (1985) 3684.
[53] V. Balzani, M.T. Indelli, M. Maestri, D. Sandrini, F. Scandola, J. Phys. Chem. 84 (1980) 852.
[54] F. Wilkinson, A. Farmilo, J. Chem. Soc. Faraday Trans. 2(74) (1978) 2083.