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Correlations of optical and thermal charge transfer

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Contents

Abstract

The relationships between the observed charge transfer absorption maxima and the independently measured free energy parameters of the constituent donor–acceptor (D/A)

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couples are contrasted for systems in which the D/A coupling is weak (as in ion pairs) to those in which it is strong (as in metal-to-ligand charge transfer systems). The general relationship between the measured parameters can be expressed as, $h\nu_{\mathrm{max}} = F\Delta E_{1/2} + \chi_{\mathrm{reorg}} - RT\ln K_{\mathrm{DA}}$, where $\Delta E_{1/2}$ is the difference between the half-wave potentials and χ_{reorg} is the reorganizational free energy of the constituent D/A couples, and K_{DA} is an equilibrium constant for the electron transfer process that relates the ground state, the excited state and the constituent D/A couples. For ion pair systems, $\Delta E_{1/2}$ can be measured directly, χ_{reorg} is often available from kinetic studies of electron transfer self-exchange reactions ($\chi^{\mathrm{ex}}_{\mathrm{reorg}} = 4\Delta G^{\ddagger}$) and K_{DA} can be replaced by the ratio of ground state and excited state ion pair association constants. For strongly coupled systems, $RT\ln K_{\mathrm{DA}}$ can be replaced by the difference of the ground state stabilization and excited state destabilization energies that result from configurational mixing between the ground and excited state. Values of χ_{reorg} are not usually known in strongly coupled systems, but plausible estimates can be based on simpler electron transfer systems. For polypyridine ligands, symmetry issues and configurational mixing between ligand components, and between different polypyridine ligands can contribute to the spectroscopy, but do not appreciably complicate the absorption maximum/electrochemical correlations. The solvent reorganizational free energy contribution to $h\nu_{\mathrm{max}}$ is expected to be small for the electrochemical correlations involving the strongly coupled systems, in part due to charge delocalization and in part due to the correction (K_{DA}) for electrochemical measurements on the constituent redox couples. Experimental data indicate that reorganizational parameters are small and only very weakly solvent dependent for the strongly coupled systems: (1) metal-to-metal charge transfer transitions in CN-bridged $\mathrm{Ru^{II}/Ru^{III}}$ complexes; and (2) metal-to-ligand charge transfer transitions in simple $\mathrm{Ru^{II}}$–polypyridine complexes.

Keywords: Charge transfer; Electron transfer; Transition metal complexes; Donor–acceptor; Electrochemical/optical correlations; Absorption band shape; Reorganizational energies; Charge transfer transition energies; Ruthenium polypyridyl complexes; Ion pairs

Nomenclature

A	electron acceptor
a	mean external radius of donor and/or acceptor
CT	charge transfer
D	electron donor
E_{AD}	vertical energy difference between an excited state potential energy minimum and the ground state
E_{DA}	vertical energy difference between the ground state potential energy minimum and the excited state; in a two state system $E_{\mathrm{DA}} > E_{\mathrm{AD}}$
E^{00}_{DA}	energy difference between the ground state and the potential energy minimum of the excited state
FC	Franck–Condon
H_{BB}	matrix element for coupling different polypyridine rings in a complex with two or more polypyridine ligands

H_{DA}	electronic matrix element for a donor/acceptor system (defined with respect to the ground state); $H_{DA} = \langle \psi_e \| H \| \psi_g \rangle$
H	Hamiltonian operator
K_{DA}	electron transfer equilibrium constant
K°_{el}	the factor of K_{DA} that arises from electrostatic repulsions or attractions
r	geometrical distance between the donor and acceptor centers
sd	standard deviation from the mean of a normal distribution
VeqES	the vibrationally excited state corresponding to a specified electronic configuration
Z_A	electrical charge on the acceptor
Z_D	electrical charge on the donor
α_{DA}	H_{AD}/E_{DA}
α_N	$\alpha_{DA}/(1+\alpha^2_{DA})^{1/2}$
ΔE_{el}	difference of inter-electronic repulsion energy between the FC state and the VeqES
$\Delta G^{\ddagger}$	activation free energy for a thermally activated electron transfer process
ΔG^{00}_{DA}	free energy difference between the ground state and the VeqES; D designates the ground state (electron centered on the donor); A designates the excited state (electron centered on the acceptor)
ΔS_{reorg}	entropy difference between the FC excited state and the VeqES
ΔS_{DA}	entropy difference between the ground state and the VeqES
ε_d	H^2_{AD}/E_{AD}; excited state destabilization energy defined for the nuclear coordinates of the excited state potential energy minimum
ε_s	H^2_{DA}/E_{DA}; ground state stabilization energy arising from configurational mixing with an excited state (or from charge delocalization)
λ_{vib}	vibrational energy difference between the FC excited state and the VeqES
λ_r	vibrational reorganizational energy for the ‘degenerate’ electron transfer between different bipyridine rings of a polypyridine complex
σ	deviation from the mean value of the distribution of $(\|\Delta G^{00}_{DA}\| + \chi_{reorg})$ as a function of solvates in fluid solution
χ_{reorg}	free energy difference between the VeqES and the FC excited state; $\chi_{reorg} = \chi_s + \chi_h$
χ_s	contribution to χ_{reorg} that arises from low frequency vibrational modes; abbreviated χ^D_s for the donor (D/D^+) and χ^A_s for the acceptor (A^-/A)
χ_h	contribution to χ_{reorg} that arises from high frequency vibrational modes

χ^{ex}_{reorg}	reorganizational free energy for a self-exchange electron transfer reaction; abbreviated χ^{D}_{r} for the donor (D/D^{+}) and χ^{A}_{r} for the acceptor (A^{-}/A); based on the electron transfer rate constants, e.g. $k^{D}_{et} = A[\exp(-\chi^{D}_{r}/4RT)]$
χ^{*}_{reorg}	the 'effective' reorganizational energy $= [h\nu_{max} - F\Delta E_{1/2}]$

Ligand abbreviations

py	pyridine
bpy	2,2′-bipyridine
dpp	2,3-bis(2′-pyridyl)pyrazine
pz	pyrazine
tpy	2,6-bis(2′-pyridyl)pyridine

1. Introduction

Insights into the properties of charge transfer excited states have been based on theoretical considerations and/or experimental correlations. Lever and co-workers have done pioneering work using each of these approaches. At present, high level theoretical calculations for transition metal complexes are approachable largely on a compound-by-compound basis, and the intercomparison of the properties of different classes of compounds can best be approached using more general, but less rigorous perturbation theory arguments. We compare selected experimental observations on the spectroscopy, the electrochemistry and the thermal kinetics of three classes of transition metal electron transfer (D/A) systems in this article. In order to accomplish these comparisons, we use perturbation theory approaches to interrelate the different kinds of measurements and the different classes of compounds. Aspects of such correlations have an extensive history [1–12], but the intercomparison of three classes of compounds provides a relatively broad view of the trends in the properties and insight into some general issues of charge transfer systems.

Lever and co-workers have presented a systematic approach to representing electrochemical measurements on coordination complexes in terms of additive contributions of a metal and its ligands [11,13,14]. This approach has recently been extended to the correlation of electrochemical parameters with charge transfer transition energies [7,11,14–17]. These approaches have been both useful and instructive. In this paper, we examine some aspects of the basic principles and some patterns of the experimental observations relevant to such spectroscopic correlations.

2. Some basic principles of photoinduced charge separation

2.1. General

The optical charge transfer (CT) absorption bands associated with the D/A moieties of a molecule vary in energy, absorptivity, bandwidth and skewness. In principle, each of these spectroscopic features is related to some combination of the structural and electronic properties of the donor and acceptor [1,3–5,18–21]. This article focuses mostly on issues related to absorption band energies of D/A systems in the condensed phase. Issues of band shape and electronic coupling (or absorptivity) are discussed to a lesser extent.

2.2. Charge transfer transition band energies

An idealized system {D,A}, composed of a well-defined electron donor, D, and a well-defined electron acceptor, A, each with approximately spherical (unstructured) orbital systems, will exhibit an absorption band corresponding to the process described in Eq. (1), where the asterisk designates an electronically and vibrationally excited system.

$$\{D^-,A\} + h\nu \rightarrow {}^*\{D,A^-\} \tag{1}$$

The CT excited state initially generated by the absorption of light is called the Franck–Condon (FC) excited state. It is the energies of FC excited states that are most often correlated with electrochemical parameters. Since only free energy quantities are measured electrochemically, the relationship of these measurements to the photonic energy of the FC state has sometimes involved discussion of entropy corrections. However, according to the FC principle, the FC excited state will have the same nuclear coordinates as the ground state. Unless there is a difference in electronic multiplicity of the ground and FC states, there will be no entropy difference between these states. Thus, the photonic energy, $h\nu_{\max}$, can be equated to a sum of free energy quantities, as in Eq. (2)

$$h\nu_{\max} = |\Delta G^{00}_{DA}| + \chi_{\text{reorg}} + \cdots \tag{2}$$

where ΔG^{00}_{DA} is the free energy difference between the ground and vibrationally equilibrated excited states, VeqES, and χ_{reorg} is the free energy difference between the FC state and the VeqES. There are some aspects of the free energy correlations that do not seem to have been generally appreciated, so a careful discussion of the issues is warranted.

The nuclei in the FC excited state generated by irradiation of a CT absorption band will not generally be at equilibrium with the new charge distribution. Nuclear relaxation of the FC state, involving bond length and bond angle changes in the molecule and translational and orientational changes in the solvent, may generate a VeqES. The difference in the energy of the FC and VeqES, λ_{vib}, will appear as heat deposited in a condensed phase environment, but this process will also generally be accompanied by an entropy change, ΔS_{reorg}, and $\chi_{\text{reorg}} = (\lambda_{\text{vib}} - T\Delta S_{\text{reorg}})$. The energy relationships, summarized in Eq. (3) (ΔE_{el} represents the relaxation of inter-electronic repulsion energy that may accompany the nuclear relaxation), are qualitatively illustrated in Fig. 1.

$$h\nu_{\max} = E_{\mathrm{DA}}^{00} + \lambda_{\mathrm{vib}} + \Delta E_{\mathrm{el}} + \cdots \tag{3}$$

Eq. (3) is a correct description of the components of the absorption energy, but the parameters on the right hand side are rarely easily accessible. Most discussions focus on the more readily measurable free energy quantities. Provided that ΔE_{el} is small, $\Delta G_{\mathrm{DA}}^{00} = (E_{\mathrm{DA}}^{00} - T\Delta S_{\mathrm{DA}}^{00})$ and $\Delta S_{\mathrm{DA}}^{00} = -\Delta S_{\mathrm{reorg}} = \Delta S_{\mathrm{DA}}$. The electrochemical measurements can be related to $\Delta G_{\mathrm{DA}}^{00}$, but not to E_{DA}^{00} unless there is a determination of ΔS_{DA}.

The final issue to be confronted with regard to Eq. (2) is the meaning of χ_{reorg}. Reorganizational free energies, $\chi_{\mathrm{reorg}}^{\mathrm{ex}}$, are reasonably well defined and well understood for bimolecular electron transfer reactions in solution [3,12,22–26]. The molecular parameters that contribute to $\chi_{\mathrm{reorg}}^{\mathrm{ex}}$ are closely related to those that contribute to χ_{reorg} since the physical processes involved are largely the same [4,5,23,24,27–29]. For example, Hush utilized this relationship in his treatment of mixed valence complexes [4,5]. However, the limits of direct comparisons of experimental data for χ_{reorg} (for the optically activated process) to $\chi_{\mathrm{reorg}}^{\mathrm{ex}}$ (for the bimolecular, thermally activated electron transfer process) have rarely been probed. If $\chi_{\mathrm{reorg}}^{\mathrm{ex}}$ is based on self-exchange electron transfer rate constants of the constituent donor D^+/D (or acceptor, A/A^-) couples, $\chi_{\mathrm{reorg}}^{\mathrm{ex}}(D) = 4\Delta G_{D}^{\ddagger}$ (where $\Delta G_{D}^{\ddagger}$ is the activation free energy for the D^+/D (or A/A^-) self-exchange electron transfer reaction), then in evaluating χ_{reorg} one must take account of the any differences in

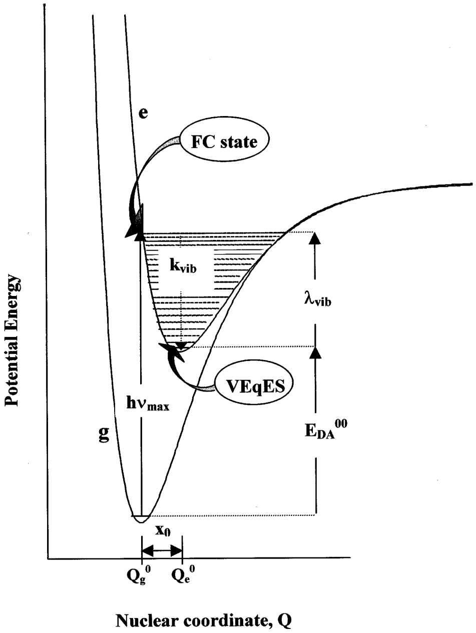

Fig. 1. Idealized, two-dimensional potential energy surfaces in the two state limit. The energy parameters are discussed in the text. The displacement parameter, x_0, is the distance between potential energy minima in the configuration space of the correlated nuclear coordinates.

the nuclear coordinates within the D/A pair and those of the separated constituents. Such differences can arise because the electronic coupling between the donor and the acceptor will result in some charge delocalization and this can result in bond length changes, changes in solvation, etc. These differences can have significant implications for the interpretation of the observed parameters.

Charge delocalization becomes important only when D/A electronic coupling becomes large. Electronic coupling is most readily discussed in terms of the perturbational mixing of diabatic (unmixed donor and acceptor) wave functions, ψ_g° and ψ_e° (g = ground state; e = product state; see Fig. 1), of a two state representation of the electron transfer reactants and products [1,8]. Electronic coupling results in the first order corrected wave functions given in Eqs. (4a) and (4b), where $\alpha_{DA} = H_{DA}/E_{DA}$ and $H_{DA} = \langle \psi_e^{\circ} | H | \psi_g^{\circ} \rangle$.

$$\psi_g = [\psi_g^{\circ} + \alpha_{DA}\psi_e^{\circ}]/(1 + \alpha_{DA}^2)^{1/2} \tag{4a}$$

$$\psi_e = [\alpha_{DA}^{*}\psi_g^{\circ} - \psi_e^{\circ}]/(1 + \alpha_{DA}^{*2})^{1/2} \tag{4b}$$

Consider the limit in which χ_{reorg} is largely due to the solvational changes that accompany the electron transfer process. For this limit, the D/A solvent reorganizational free energy is the average of the component, D^+/D and A/A^- electron transfer self-exchange solvent reorganizational free energies, $\chi_s^{DA}(D/A) = 1/2[\chi_s^{ex}(D^+/D) + \chi_s^{ex}(A/A^-)]$. If the solvent reorganizational free energy is given by a function of the form, $\chi_s^{ex} = C_s(\Delta Z)(a^{-1} - r^{-1})$ [23,24] (C_s is a constant, ΔZ represents the electrical charge dependent part of χ_s, a is a parameter based on the external dimensions of the molecule and r is the effective distance for the transfer of an electron), then the effects of the charge delocalization that result from D/A coupling can be manifested by changes of ΔZ and/or of r. The effect of charge delocalization (of a fraction, α_N^2 of an electron; $\alpha_N = \alpha_{DA}/[1 + \alpha_{DA}]^{1/2}$; the normalization is important when α_{DA} is large) based on a simple electrostatic solvational model (solvation energy of each ion is proportional to Z^2/a [30]) leads to a solvation energy change for a one electron transfer process, Eq. (5), which is proportional to $(2Z_D + 1 - 2\alpha_N^2)$ at the donor and $(-2Z_A + 1 - 2\alpha_N^2)$ at the acceptor.

$$\{D^{(Z_D + \alpha_N^2)}, A^{(Z_A - \alpha_N^2)}\} + h\nu \rightarrow \{D^{(Z_D + \alpha_N^2 - 1)}, A^{(Z_A - \alpha_N^2 + 1)}\} \tag{5}$$

This leads to a reorganizational contribution in the D/A pair of $\chi_s \cong \chi_s^{DA}(1 - 2\alpha_N^2)$. An additional contribution arises from the effect of charge delocalization on r. The effective electron transfer distance is smaller than r by approximately $(-2\alpha_N^2 r)$ [31]. The combination of these two contributions leads to $\chi_s = \chi_s^{ex}(1 - 2\alpha_N^2)$ when $r \gg a$, and $\chi_s \to 0$ for $r \to a$ (i.e. for the change of dipole small compared to the external molecular dimensions). The actual situation is no doubt more complicated, but the arguments presented here should be appropriate for the general trends.

The rate at which vibrational energy in the electronically excited system is converted into heat in the solvent medium appears to vary with the size of the molecular vibrational quanta and with other factors governing the coupling of the molecular vibrational motion to the solvent vibrational modes [28,32–35]. The dynamics of these relaxation processes are beyond the scope of this article.

2.3. CT absorption bandwidths

The absorption bandwidth can in principle be related to the reorganizational energy [4,5,27,36]. This relationship is generally somewhat complicated in condensed media [37,38], and absorption bandwidths are generally observed to be broader in solution than in the crystalline solid or in the gas phase. Contributions of the solvent to the bandwidth can arise: (a) from solvent reorganizational energies; and/or (b) if $\Delta G^{00}_{\mathrm{DA}}$ and χ_{reorg} vary with the solvent environment; if the species in solution have a distribution of solvent environments then the measured quantities are averages for the distribution of solvates. For the deviations of these quantities given by $\sigma = \sigma_{\Delta G} + \sigma_{\chi}$, and for a gaussian absorption band shape (for example, $\mathrm{A}(h\nu_{\mathrm{abs}}) = \mathrm{A}_0 \exp[-(\Delta G^{00}_{\mathrm{DA}} + \chi_{\mathrm{reorg}} \pm \sigma - h\nu_{\mathrm{abs}})^2/4k_{\mathrm{B}}T\chi_{\mathrm{s}}]$; see also Eq. (7)) the bandwidth (full-width at half-height) is represented by Eq. (6) [18,39,40]. Since $\Delta G^{00}_{\mathrm{DA}}$ and χ_{reorg} may vary differently, but not independently, with changes of solvation, the distribution of deviations from the mean value of $(\Delta G^{00}_{\mathrm{DA}} + \chi_{\mathrm{reorg}})$ need not be a normal distribution

$$\Delta\nu_{1/2} \cong 2\sigma + 4(k_{\mathrm{B}}T\chi_s \ln 2)^{1/2} \tag{6}$$

For a normal distribution of deviations from the mean, $\sigma = \mathrm{sd}(\ln 2)^{1/2}$ where sd is the standard deviation of the normal distribution. As a result of the distribution of solvates, and since $\Delta G^{00}_{\mathrm{DA}}$ for an oxidation reduction reaction is typically strongly solvent dependent, the absorption bandwidth is rarely a reliable, quantitative measure of the reorganizational energy. In systems in which $\Delta G^{00}_{\mathrm{DA}}$ is solvent dependent, band shape models that omit this dependence may not yield quantitative results. On the other hand, there is often some compensation for the solvent dependence of $\Delta G^{00}_{\mathrm{DA}}$ by the solvent dependence of χ_{reorg} (see above comments on ΔS_{DA}), and if there is a corresponding anti-correlation in the variations of $\sigma_{\Delta G}$ and σ_{χ}, then bandwidths can be useful for relative and qualitative discussions. Other factors, such as unresolved electronic or vibronic components can also contribute to the experimental bandwidths.

2.4. Absorption band skewness

The oxidation or reduction of molecular species typically results in bond length and/or bond angle changes. If these structural changes correspond to distortions (relative to the initial state) in vibrational modes, ν_{h}, for which $h\nu_{\mathrm{h}} > 4k_{\mathrm{B}}T$, then the optical absorption may exhibit components that correspond to the successive population of the high frequency vibrational modes in the excited state [11]. For a single contributing high frequency mode and a continuum of low frequency modes (for simplicity attributed to the solvent, s), ν_{s}, so that $\chi_{\mathrm{reorg}} = (\chi_{\mathrm{h}} + \chi_{\mathrm{s}})$, then Eq. (7) is a useful approximation for the absorption band shape [41,42].

$$\varepsilon(\nu_{\mathrm{abs}}) = \frac{8N_{\mathrm{A}}\pi^3}{3000h^2c\nu_{\mathrm{abs}} \ln 10} n^3 H^2_{\mathrm{DA}}(\Delta\mu_{\mathrm{DA}})^2(\mathrm{FC}) \tag{7}$$

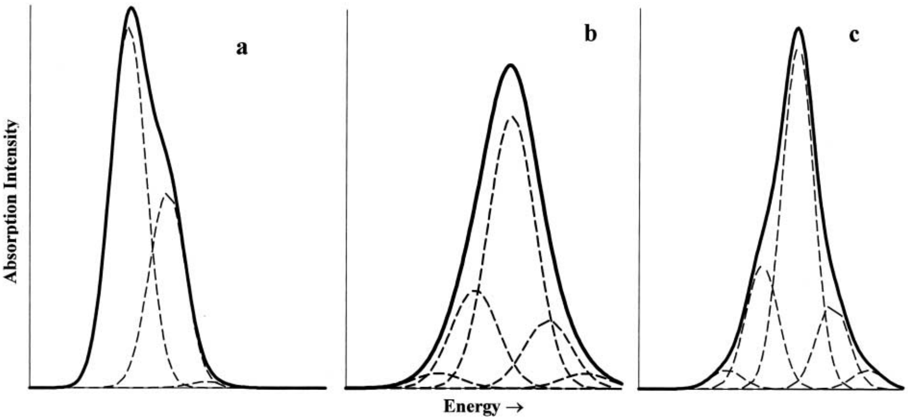

Fig. 2. Illustrations of the different limits for the contributions of high frequency vibrational modes to the absorption band shape (for emission band shape the energy scale would be reversed). The weights of the individual vibronic components, dashed lines, are based on Eq. (5) with (a) $\chi_i/\chi_h = 2$; (b) $\chi_l/\chi_h = 1/2$; and (c) $\chi_l/\chi_h = 1/2$. The bandwidths are the same in (a) and (c) and twice as large in (b). Note that $h\nu_{max}$ contains a contribution from χ_h for (b) and (c) but not for (a). Vibrational quanta ($j = 0,1,2,\ldots$) increase from left to right.

$$(\mathrm{FC}) = \sum_j F_j \exp[-(|\Delta G^{00}_{\mathrm{DA}}| - h\nu_{\mathrm{abs}} + jh\nu_{\mathrm{h}} + \chi_{\mathrm{s}})^2/4\chi_{\mathrm{s}}k_{\mathrm{B}}T]$$

$$F_j = S^j[\exp(-S^j[\exp(-S^j)]]/[j!(4\pi\chi_{\mathrm{s}}k_{\mathrm{B}}T)]$$

$$S = \chi_{\mathrm{h}}/h\nu_{\mathrm{h}}$$

Here $\varepsilon(\nu_{\mathrm{abs}})$ is the molar absorptivity at the frequency ν_{abs}, n the index of refraction, $H_{\mathrm{DA}} = \langle\psi_{\mathrm{D}}|H|\psi_{\mathrm{A}}\rangle$ the electronic coupling matrix element, ψ_{K} the respective wave functions and (FC) is the Franck–Condon factor. The evaluation of the maximum of $[\varepsilon(\nu_{\mathrm{abs}})]\nu_{\mathrm{abs}}$ with respect to $h\nu_{\mathrm{abs}}$ leads to Eqs. (2) and (3). Two limiting cases must be considered if high frequency vibrational modes make a significant contribution to the excited state distortion: (a) the distortion in these modes is small ($\chi_{\mathrm{h}} < \chi_{\mathrm{s}}$), $S \ll 1$, and $h\nu_{\mathrm{max}}$ is given by Eq. (8a);

$$h\nu_{\mathrm{max}} \cong \Delta G^{00}_{\mathrm{DA}}| - \chi_{\mathrm{s}} + \cdots \tag{8a}$$

and (b) the distortion in these modes is large, $S > 1$, and $h\nu_{\mathrm{max}}$ is given by Eq. (8b).

$$h\nu_{\mathrm{max}} \cong \Delta G^{00}_{\mathrm{DA}}| - \chi_{\mathrm{s}} + \chi_{\mathrm{h}} - \cdots \tag{8b}$$

The absorption band will be unsymmetrical in the first limit, with somewhat higher intensities on the high energy side of the absorption maximum than on the low energy side. These limits are illustrated in Fig. 2. When Eq. (8b) applies and both χ_{s} and χ_{h} make significant contributions, Eq. (6) must be modified as in Eq. (9) [27].

$$\Delta\nu_{1/2} \cong 2\sigma + 2[(4k_{\mathrm{B}}T\chi_{\mathrm{reorg}} + h\nu_h\chi_h)\ln 2]^{1/2} \tag{9}$$

2.5. The electrochemical connection

Since $\Delta G^{00}_{\mathrm{BC}} = -F\Delta E_{1/2}(\mathrm{B/C}) = -F[E_{1/2}(\mathrm{C/C^-}) - E_{1/2}(\mathrm{B^+/B})]$ (where F = Faraday's constant) for Eq. (10), and since the CT absorption induces a related charge transfer,

$$\mathrm{B} + \mathrm{C} \rightleftarrows \mathrm{B^+} + \mathrm{C^-} \tag{10}$$

one expects a correlation between $h\nu_{\max}$ and $F\Delta E_{1/2}(\mathrm{B/C})$. However, the photochemical process, Eq. (11), differs from the thermal, Eqs. (8a) and (8b), and these processes are

$$(\mathrm{D}) - (\mathrm{A}) + h\nu \rightarrow (\mathrm{D^+}) - (\mathrm{A^-}) \tag{11}$$

thermochemically related by means of the electron transfer equilibrium in Eq. (12)

$$(\mathrm{D}) - (\mathrm{A}) + (\mathrm{D^+}) - (\mathrm{A^-}) \overset{K_{\mathrm{DA}}}{\rightleftarrows} (\mathrm{D^+}) - (\mathrm{A}) + (\mathrm{D}) - (\mathrm{A^-}) \tag{12}$$

[11,20]. Thus, $\Delta G^{00}_{\mathrm{DA}} = (F\Delta E_{1/2}(\mathrm{D/A}) + RT \ln K_{\mathrm{DA}})$, and Eq. (2) can be rewritten as in Eq. (13). In a typical donor/acceptor system, the species (D)–(A) will be stabilized

$$h\nu_{\max} \cong F\Delta E_{1/2}(\mathrm{D/A}) + RT \ln K_{\mathrm{DA}} + \chi_{\mathrm{reorg}} + \cdots \tag{13}$$

with respect to the individual (D) and (A) constituents by an amount $\varepsilon_{\mathrm{s}} = H^2_{\mathrm{DA}}/E_{\mathrm{DA}}$ (E_{DA} is the vertical energy difference between the donor and acceptor states) and the $(\mathrm{D^+})$–$(\mathrm{A^-})$ species is similarly destabilized with $\varepsilon_{\mathrm{d}} = H^2_{\mathrm{AD}}/E_{\mathrm{AD}}$ [1]. Since the species in Eq. (11) are either equilibrium, or vibrationally equilibrated species, $E_{\mathrm{AD}} < E_{\mathrm{DA}}$ and $\varepsilon_{\mathrm{d}} > \varepsilon_{\mathrm{a}}$. To a good approximation (assuming that $H_{\mathrm{DA}} = H_{\mathrm{AD}}$), Eq. (14) gives the free energy contribution resulting from Eq. (12),

$$RT \ln K_{\mathrm{DA}} = \varepsilon_{\mathrm{s}} - \varepsilon_{\mathrm{d}} + RT \ln K^{\circ}_{\mathrm{el}} \tag{14}$$

where K°_{el} contains the electrostatic contribution to K_{DA}. For harmonic potential energy surfaces with similar excited and ground state force constants, $\varepsilon_{\mathrm{s}} \cong H^2_{\mathrm{DA}}/(|\Delta G^{00}_{\mathrm{DA}}| + \chi_{\mathrm{reorg}})$ and $\varepsilon_{\mathrm{d}} \cong H^2_{\mathrm{DA}}/(|\Delta G^{00}_{\mathrm{DA}}| - \chi_{\mathrm{reorg}})$, and if $|\Delta G^{00}_{\mathrm{DA}}| \gg \chi_{\mathrm{reorg}}$, $(\varepsilon_{\mathrm{s}} - \varepsilon_{\mathrm{d}}) \cong -2\alpha^2_{\mathrm{N}}\chi_{\mathrm{reorg}}[1 + (\chi_{\mathrm{reorg}}/\Delta G^{00}_{\mathrm{DA}}) + \cdots]$; thus, $RT \ln K_{\mathrm{DA}} \cong (-2\alpha^2_{\mathrm{N}}\chi_{\mathrm{reorg}} + RT \ln K^{\circ}_{\mathrm{el}} + \cdots)$. This term can be important for strongly coupled systems. In such systems the best optical/thermal correlations should be generated using Eq. (15).

$$h\nu_{\max} \cong F\Delta E_{1/2}(\mathrm{D/A}) + \chi_{\mathrm{reorg}}(1 - 2\alpha^2_{\mathrm{N}} - 2\chi_{\mathrm{reorg}}\alpha^2_{\mathrm{N}}/\Delta G^{00}_{\mathrm{DA}}) + RT \ln K^{\circ}_{\mathrm{el}} + \cdots) \tag{15}$$

Note that χ_{reorg} in Eq. (15) is the parameter from Eq. (2) and not the average of constituent couple self-exchange reorganizational free energies. For correlations involving the latter an additional correction is necessary as discussed in Section 2.2. A stabilization energy contribution from D/A coupling also arises in $F\Delta E_{1/2}(\mathrm{D/A})$. This is $2\varepsilon_{\mathrm{s}}$ for a simple two state system. In the limit that α_{DA} is small, and for χ_{reorg} the average of the reorganizational free energies of the component redox couples ($\mathrm{D^+/D}$ and $\mathrm{A/A^-}$), the simple two state limit implies that the free energy contributions to $h\nu_{\max}$ can be separated into the sum of the contributions of D and A, Eq. (16). When α_{DA} is large,

$$F(\mathrm{D}) = [-FE_{1/2}(\mathrm{D}^+|\mathrm{D}) + \chi_{\mathrm{r}}^{\mathrm{D}}/2] \quad \text{and} \quad F(\mathrm{A}) = [FE_{1/2}(\mathrm{A}|\mathrm{A}^-) + \chi_{\mathrm{r}}^{\mathrm{A}}/2] \tag{16}$$

the separation into D and A contributions is not accurate unless there is a cancellation of terms containing α_{DA}^2. Experimental information on several weakly and strongly coupled systems (small and large α_{DA}) is examined in this article.

3. The correlation of optical and thermal energies in weakly coupled systems ($\alpha_{\mathrm{DA}}^2 < 0.1$)

3.1. Ion pair charge transfer systems

The ion pair species considered here, such as $\{\mathrm{Ru(NH_3)_6,I^-}\}$, are not covalently linked and are at equilibrium with the constituent ions in solution, Eq. (17).

$$M(L)_{\mathrm{r}}^{m+} + X^{n-} \rightleftarrows \{M(L)_{\mathrm{r}}^{m+}, X^{n-}\} \tag{17}$$

Due to the relatively large separation of D and A, and the effects of thermal averaging of the distribution of transition metal complex ion pair geometries, the only orbital distinctions relevant to these systems are for electron holes in the dσ and dπ orbital subsets. As a result the physical properties of these ion pairs are easily considered as a slightly (or perturbationally) altered superposition of the properties of those constituents: $h\nu_{\max} = F(\mathrm{A}) + F(\mathrm{D})$; see Table 1. The half-wave potentials of these ion pairs are related to those of the constituent ions through the ion pair association constants, K_0 and $^*K_0$, of the respective ground and electron transfer excited states, and K_{DA} in Eq. (14) may be replaced by $K_0/^*K_0$ when $\Delta E_{1/2}$ corresponds to the constituent half-wave potentials, Eq. (18). This 'work term' correction, $RT\ln(^*K_0/K_0)$, is small and ignored in the discussion below

$$\Delta G_{\mathrm{DA}}^{00} = FE_{1/2}(\mathrm{D}^+|\mathrm{D}) - FE_{1/2}(\mathrm{A}|\mathrm{A}^-) + RT\ln(^*K_0/K_0) \tag{18}$$

There have been several general treatments and discussions of ion pair charge transfer (IPCT) spectra [3,7,11,18,43–46]. Representative samples of IPCT spectra have been assembled elsewhere [7,18]. Table 1 summaries the electrode potentials [47–55] and electron transfer reorganizational free energies [19,25,48,49,51,52,54–59] for the constituent couples of some of these ion pairs, and these parameters have been used (Fig. 3) to obtain each constituent's contribution to an ion pair absorption maximum. The reorganizational free energies, χ_{reorg}, in Table 1 were obtained from the reported, experimental rate constants for self-exchange reactions (Eq. (19)), except those for the halides and NCS$^-$ for which best-fit (to the IPCT data for Ru$^{\mathrm{III}}$ ion pairs) values have been used.

$$M(L)_t^{m+} + {}^*M(L)_t^{(m+1)+} \rightleftarrows M(L)_t^{(m+1)+} + {}^*M(L)_t^{m+} \tag{19}$$

The observed IPCT energies for Ru$^{\mathrm{III}}$, Co$^{\mathrm{III}}$ and $\mathrm{Fe(CN)_6^{3-}}$ acceptors are reasonably predicted by the sum of the difference in electrode potentials and the average of the reorganizational free energies ($\chi_{\text{reorg}}^{\text{ex}} = 4\Delta G^{\ddagger}$) of the self-exchange reactions of the constituent couples; Eq. (16) and Fig. 3. Excluding the halides, the overall correlation based on Eqs. (3) and (18) has a slope of 0.87 ± 0.06, an intercept of $(2.0 \pm 1.2) \times 10^3$ cm^{-1} with $r^2 = 0.91$ (including halides for all but the reference systems results in a slope of 0.95 ± 0.04, an intercept of 1.2 ± 1.2 and $r^2 = 0.94$; Fig. 3). This can be considered as a good confirmation of this approach since the experimental parameters used in the correlation were based on measurements of three very different quantities, and the measurements were performed in about 30 different laboratories. There are some apparently systematic deviations from the general correlation: (a) the $[\text{Os(CN)}_6]^{4-}$ donors consistently show the largest positive differences ($\Delta h\nu_{\max}$) between $h\nu_{\max}$(obsd) and $h\nu_{\max}$(calcd), about 3×10^3

Table 1
Electron transfer parameters for use in IPCT correlations [a]

Couple	E_f [b] (V)	$\chi_{\text{reorg}}^{\text{ex}}$ [c] (cm^{-1}/10^3)	$r_{\text{D(A)}}$ [d] (Å)	F(A) (cm^{-1}/10^3)	F(D) (cm^{-1}/10^3)
$\text{Ru(NH}_3)_6^{3+,2+}$	0.06 [47,59]	13.64 [59]	3.35	6.34	7.30
$\text{Ru(en)}_3^{3+,2+}$	0.21 [55,59]	13.31 [59]	3.7	4.96	8.35
$\text{Ru(NH}_3)_5(\text{py})^{3+,2+}$	0.3	10.3[85]	3.8	2.73	7.57
$\text{Ru(NH}_3)_4(\text{bpy})^{3+,2+}$	0.46 [40]	10.4[85]	4.4	1.49	8.9
$\text{Fe(CN)}_6^{3-,4-}$	0.358 [48]	10.7 [49]	4.6	2.46	8.23
$\text{Ru(CN)}_6^{3-,4-}$	0.92 [49]	10.4 [49]	4.7	−2.22	12.62
$\text{Os(CN)}_6^{3-,4-}$	0.63 [49]	10.4 [49]	4.7	0.12	10.28
$\text{Mo(CN)}_8^{3-,4-}$	0.726 [48]	~10 [48]	…	~−0.86	~10.8
$\text{W(CN)}_8^{3-,4-}$	0.456 [48]	~10 [48]	…	~1.3	~8.7
$\text{Co(NH}_3)_6^{3+,2+}$	−0.06 [47]	35.11 [50,58]	3.3	18.0	17.1
$\text{Co(en)}_3^{3+,2+}$	−0.21 [58]	30.32 [57]	3.65	16.85	13.45
$\text{Co(sep)}^{3+,2+}$	−0.30 [51]	21.56 [51]	4.1	13.2	8.4
$\text{Co([9]aneN}_4)^{3+,2+}$	−0.40 [52]	25.81 [52]	4.4	15.78	9.8
$\text{Cl}^{0,1-}$	2.35 [53]	19.42 [e]		−9.2	28.7
$\text{Br}^{0,1-}$	1.86 [53]	19.32 [e]		−5.3	24.7
$\text{I}^{0,1-}$	1.27 [53]	14.42 [e]		−3.0	17.4
$\text{NCS}^{0,1-}$	1.57 [53]	15.6 [e]		−4.9	20.5

[a] All values refer to aqueous solutions.

[b] Formal potentials referenced to NHE from tabulations [7,55] of the references indicated.

[c] Values for the reorganizational free energies based on observed rate constants for self-exchange reactions (Eq. (19)) of the couples noted, except (for halides) as indicated: $k_{\text{exch}} = K_0 \nu_{\text{eff}} \exp(-\chi_{\text{r}}^{\text{th}}/4k_{\text{B}}T)$. Values of ν_{eff} vary depending on the contributions to $\chi_{\text{r}}^{\text{th}}$, $\nu_{\text{eff}}^2 = (\nu_{\text{s}}^2\chi_{\text{s}}^{\text{th}} + \nu_{\text{h}}^2\chi_{\text{h}}^{\text{th}})/(\chi_{\text{s}}^{\text{th}} + \chi_{\text{h}}^{\text{th}})$ [28]. $K_0 = (4/3)\pi(r_{\text{D(A)}})^3 N_{\text{A}} \exp(-\delta) \times 10^3$; $\delta = (Z_{\text{D}}Z_{\text{A}}e^2/\varepsilon k_{\text{B}}T)[r_{\text{DA}}^{-1} - \kappa/(1+\kappa r_{\text{DA}})]$; $\kappa = (8\pi N_{\text{A}}e^2\mu/10^3\varepsilon k_{\text{B}}T)$. Where N_{A} is Avagadro's number, e is the electronic charge, ε is the solvent dielectric constant, Z_{D} and Z_{A} are the formal charges of the donor and acceptor and μ is the ionic strength.

[d] Values based on mean van der Waals radii.

[e] Value based on fit to the $\{\text{Ru(NH}_3)_6^{3+},\text{X}^-\}$ IPCT absorption.

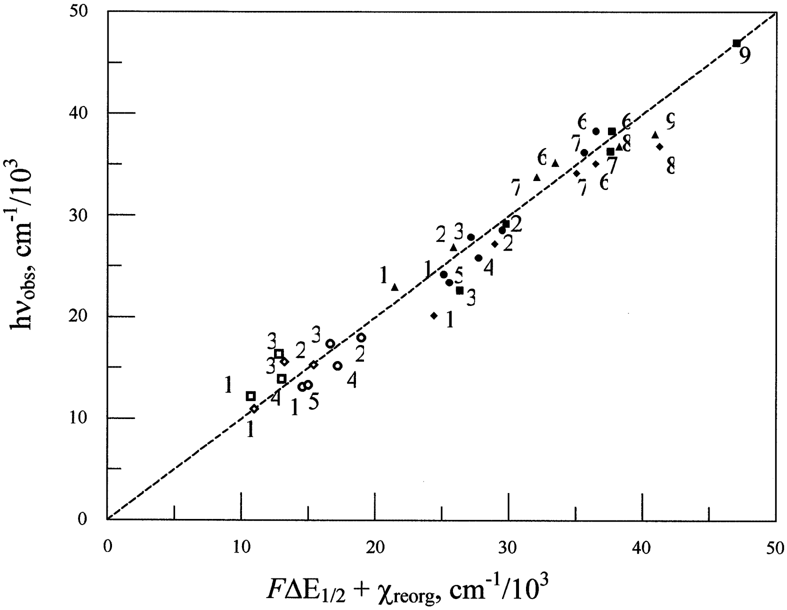

Fig. 3. Comparison of IPCT absorption maxima with the free energy quantities: $\Delta E_{1/2} = E_{1/2}(D^+/D) - E_{1/2}(A/A^-)$; $\chi_{reorg} = 4\Delta G^\ddagger$ where $\Delta G^\ddagger$ is the constituent self-exchange electron transfer reaction activation free energy (except for halide donors which are fitted to Ru^{III}/X$^-$ IPCT spectra). Acceptors: $Co(NH_3)_6^{3+}$, ■; $Co(en)_3^{3+}$, ●; $Co(sep)^{3+}$, ▲; $Co([9]aneN_4)_2^{3+}$, ◆; $Ru(NH_3)_6^{3+}$, ○; $Ru(NH_3)_5py^{3+}$, ◇; $Fe(CN)_6^{3-}$, □. Donors: $Fe(CN)_6^{4-}$, 1; $Ru(CN)_6^{4-}$, 2; $Os(CN)_6^{4-}$, 3; $Mo(CN)_8^{4-}$, 4; $W(CN)_8^{4-}$, 5; NCS$^-$, 6; I$^-$, 7; Br$^-$, 8; and Cl$^-$, 9.

cm^{-1}, suggesting either a systematic measurement error or some unique contribution (such as spin–orbit coupling) to at least one, but not all of the parameters listed in Table 2 for this complex; (b) the values of $\Delta h\nu_{max}$ are consistently more positive for $[Fe(CN)_6]^{4-}$ and for $[Co(sep)]^{3+}$ than for the other acceptors; (c) in general the values of $\Delta h\nu_{max}$ are more negative for Co^{III} acceptors (by about 1×10^3 cm^{-1}) than for dπ acceptors (the correlation line for all of the Co^{III} acceptors except $[Co(sep)]^{3+}$ has a slope of 1.3 ± 0.3 and an intercept of $-10 \pm 5 \times 10^3$ cm^{-1}). It is likely that some of these deviations reflect inconsistencies and uncertainties in the parameters used (these were often obtained using different medium conditions, and some involve spectral deconvolutions of broad, weak absorption bands).

The near consistency of the ion pairs containing Co^{III} acceptors with the overall correlation in Fig. 3 is not entirely expected. For all of the complexes considered, the spin allowed electronic IPCT transition will generate a low spin Co^{II} complex in (^2E_g in O_h symmetry). In contrast, the equilibrium Co^{II} species involved in the electrochemical and the self-exchange kinetic measurements is a high spin complex ($^4T_{1g}$ in O_h symmetry). That these systems correlate reasonably well with those of the other acceptors suggests that the half-wave potentials are more negative and the

Table 2
Charge transfer properties of some simple cyanide-bridged complexes

Complex	Solvent	$E_{1/2}(\mathrm{Ru(PP)})^{3+,2+}$ (V vs SCE)	$E_{1/2}(\mathrm{Ru(NH_3)_5})^{3+,2+}$ (V vs SCE)	$h\nu_{\max}$ ($\mathrm{cm^{-1}/10^3}$)	$F\Delta E_{1/2}$ ($\mathrm{cm^{-1}/10^3}$)	$(h\nu_{\max} - F\Delta E_{1/2})$ ($\mathrm{cm^{-1}/10^3}$)	References
$[(\mathrm{bpy})_2\mathrm{Ru(CN)}(\mathrm{CNRu(NH_3)})]^{3+}$	CH_3CN	+1.16	−0.023	14.41	9.52	4.9	[60]
	H_2O	+1.16	−0.12 ± 0.01	14.29 (4.5)	10.41	3.4	[40]
$[(\mathrm{tpy})(\mathrm{bpy})\mathrm{Ru(CNRu(NH_3)_5]^{4+}}$	CH_3CN	+1.24	+0.045	14.29	9.60	4.7	[40]
	H_2O	+1.09	−0.09 ± 0.01	14.29 (4.9)	9.60	4.7	[40,60]
$[(\mathrm{py})_4\mathrm{Ru(CN)}(\mathrm{CNRu(NH_3)_5})]^{3+}$	CH_3CN	+1.09	+0.09	11.90	8.07	3.9	[40,61]
	H_2O	+1.02	−0.12	13.42	9.20	4.2	[40,61]
$[\{(\mathrm{tpy})(\mathrm{bpy})\mathrm{Ru}\}_2\mathrm{CN}]^{4+}$	CH_3CN	+1.41 [a]	+1.00 [b]		3.2	(4.1) [c]	[86]
	H_2O			7.3 (3.7)			[86]

[a] $[\{(\mathrm{tpy})(\mathrm{bpy})\mathrm{Ru}\}_2\mathrm{CN}]^{5+,6+}$.

[b] $[\{(\mathrm{tpy})(\mathrm{bpy})\mathrm{Ru}\}_2\mathrm{CN}]^{4+,5+}$.

[c] $h\nu_{\max}(\mathrm{H_2O}) - F\Delta E_{1/2}(\mathrm{CH_3CN})$.

self-exchange rate constants are larger (i.e. the reorganizational energies are smaller) for the excited state couples involving low spin Co^{II} than for their high spin ground states, and that these differences very nearly cancel in the correlation in Fig. 3.

4. The correlation of optical and thermal energies in strongly coupled systems ($\alpha^2_{DA} > 0.1$)

4.1. General comments and contrasts to the weakly coupled limit

In the preceding section we have in effect set $K_{DA} = 1$ and treated only the corrections of the half-wave potentials that are expected to accompany ion pair formation. More careful treatments are required for strongly coupled systems, since values of α_{DA} may be large (see Eq. (15)). When the electrode potentials of only the donor (or only the acceptor) are used in such correlations, in place of $F\Delta E_{1/2}(D/A)$, then the correlations are further complicated by the systematic variations in the contributions ε_s to $E_{1/2}(A|A^-)$ (or to $E_{1/2}(D^+|D)$ if the correlation is with a series of acceptors). Consider, for example, a series of closely related donor metal complexes (D) with a common acceptor ligand (A). Then the half-wave potentials of both the metal complexes and the ligands will contain contributions, $\pm\varepsilon_s$ in a standard perturbation theory treatment, as a consequence of the mixing of donor and acceptor configurations; Eqs. (20a) and (20b) (the $E^\circ_{1/2}$ are values of half-wave potentials in the absence of D/A mixing).

$$(D) - (A) + e^- \rightleftarrows (D) - (A^-), \quad E_{1/2}(A|A^-) = E^\circ_{1/2}(A|A^-) - \varepsilon_s/F \tag{20a}$$

$$(D^+) - (A) + e^- \rightleftarrows (D) - (A), \quad E_{1/2}(D^+|D) = E^\circ_{1/2}(D^+|D) + \varepsilon_s/F \tag{20b}$$

The correlation of $h\nu_{max}$ with $E_{1/2}(D^+/D)$ has the effect of adding a term in ε_s to Eq. (13), as illustrated in Eq. (21).

$$\begin{aligned} h\nu_{max} &\cong [-FE^\circ_{1/2}(A|A^-) + \varepsilon_s] + FE_{1/2}(D^+|D) + RT\ln K_{DA} + \chi_{reorg} + \cdots \\ &\cong [-FE^\circ_{1/2}(A|A^-) + \chi^A_r/2] + [FE_{1/2}(D^+|D) + \chi^D_r/2] + \varepsilon_s + RT\ln K_{DA} \end{aligned} \tag{21}$$

The quantities in square brackets in Eq. (21) are functions of only the acceptor and of only the donor (the F(A) and F(D) quantities of Table 1), respectively, and the remaining terms depend on both the donor and acceptor. If we set $\varepsilon_s(D/A) = H^2_{DA}/(E_{D_RA} + \Delta E_{D_RD})$, $FE_{1/2}(D^+|D) \cong F(E_{1/2}(D^+_R|D_R) + \Delta E_{1/2}(D_R|D))$ and $\varepsilon_s = \varepsilon_s(D_R)[1 - F\Delta E_{1/2}(D_R|D)/E_{DA}(R)]$ (for some reference compound D_R) and assume that H_{DA} and χ_{reorg} are invariant in a related series of complexes, then the substitution of Eq. (14) into Eq. (21) and neglecting K_{el} leads to the relationship between variations in the absorption maximum and the varying donor potentials in Eq. (22) where $W(A,D_R)$ contains terms

$$\begin{aligned} \nu_{\max} &\cong \{FE_{1/2}(\mathrm{D_R^+}|\mathrm{D}) - FE_{1/2}(\mathrm{A}|\mathrm{A^-}) + \varepsilon_s(\mathrm{D_R}) + \ln K_{\mathrm{DA}} + \chi_{\mathrm{reorg}}(\mathrm{D_R/A})\} \\ &\quad + F\Delta E_{1/2}(\mathrm{D_R/D}) + \varepsilon_s(\mathrm{D}) - \varepsilon(\mathrm{D_R}) + \cdots \\ &\cong W(\mathrm{A,D_R}) + F\Delta E_{1/2}(\mathrm{D_R/D})[1 - (\alpha_N^{\circ})^2 + 2\chi_{\mathrm{reorg}}(\alpha_{\mathrm{N}}^{\circ})^2/E_{\mathrm{D_RD}}] + \cdots \end{aligned} \tag{22}$$

independent of $F\Delta E_{1/2}(\mathrm{D_R/D})$ and $\alpha_N^{\circ} = H_{\mathrm{DA}}/E_{\mathrm{D_RA}}/[1 + \{H_{\mathrm{DA}}/E_{\mathrm{D_RA}}\}^2]^{1/2}$. If χ_{reorg} and α_{N} are constant through the series of compounds (independent of $\Delta E_{1/2}(\mathrm{D_R}|\mathrm{D})$), then the slope of the correlation of $h\nu_{\max}$ with $FE_{1/2}(\mathrm{D^+}|\mathrm{D})$ is approximately given by $(1 - \alpha_{\mathrm{N}}^2)$. Similarly, for the donor held constant and the acceptor varied, the correlation should have a slope of approximately $-(1 + \alpha_{\mathrm{N}}^{\circ 2})$.

4.2. Metal-to-metal charge transfer in cyanide bridged bimetallic complexes

We have examined the metal-to-metal charge transfer behavior in some simple cyanide-bridged complexes [31,39,60–67]. These complexes contrast to the IPCT systems in that the electronic coupling is large enough that α_{DA} can be as large as ~ 0.2 [31], and they can be used to illustrate some properties generally expected of strongly coupled systems. The compounds included in these studies were of the types $[\mathrm{L_5M(CNRu(NH_3)_5)}]^{m+}$ and *cis*- or *trans*-$[\mathrm{L_4M(CNRu(NH_3)_5)_2}]^{n+}$. The non-bridging ligands (L) were pyridine, polypyridyls, tetraazamacrocycles, am(m)ines or $\mathrm{CN^-}$ (there was no more than one non-bridging cyanide in these series of complexes). For these complexes, $h\nu_{\max}$ has been shown to correlate with $E_{1/2}(\mathrm{Ru(NH_3)_5^{3+,2+}})$ through the perturbational contributions to ε_s [31] as in Eq. (21). The correlations employed did not consider the contributions of $RT \ln K_{\mathrm{DA}}$, but this contribution should be small since $\chi_{\mathrm{reorg}} \ll h\nu_{\max}$ for these complexes. It is instructive to consider in more detail the subset of complexes in which $\mathrm{CN^-}$ bridges a $\mathrm{Ru^{II}}$ to one $\mathrm{Ru^{III}}$ center. Relevant data [40] are summarized in Table 2 for $[(\mathrm{bpy})_2\mathrm{Ru(CN)(CNRu(NH_3)_5)}]^{3+}$, $[(\mathrm{bpy})(\mathrm{tpy})\mathrm{Ru(CNRu(NH_3)_5)}]^{4+}$ and *trans*-$[(\mathrm{py})_4\mathrm{Ru(CN)(CNRu(NH_3)_5)}]^{3+}$. The MMCT bands in these complexes are intense ($\varepsilon_{\max} \sim 4 \times 10^4\ \mathrm{cm^{-1}\ M^{-1}}$), broad ($\Delta\nu_{1/2} \sim 5 \times 10^3\ \mathrm{cm^{-1}}$) and nearly gaussian in shape with no evident vibronic structure. The quantity $\chi_{\mathrm{r}}^* = (h\nu_{\max} - F\Delta E_{1/2})$ is nearly constant for these compounds, with an overall average of $(4.4 \pm 0.4) \times 10^3\ \mathrm{cm^{-1}}$ (average of spectra in water and in acetonitrile); in the different solvents the averages are $(4.5 \pm 0.4) \times 10^3\ \mathrm{cm^{-1}}$ (acetonitrile) and $(4.3 \pm 0.3) \times 10^3\ \mathrm{cm^{-1}}$ (water); the same value is found for $[\{(\mathrm{tpy})(\mathrm{bpy})\mathrm{Ru}\}_2\mathrm{CN}]^{4+}$. Some effects of a non-bridging cyanide or of *cis*- compared to *trans*-geometry may be present, but they are within the one standard deviation error limits of the overall average. Water, on the basis of dielectric behavior or of specific solvational effects, is expected to have a larger reorganizational energy than is acetonitrile. Within experimental uncertainties these CN-bridged bimetallic complexes appear to give a value for the reorganizational free energy that is independent of solvent or complex size. This is not in accord with expectations based on $\chi_{\mathrm{s}}^{\mathrm{ex}} = 4\Delta G^{\ddagger}$. It appears that the value of χ_{reorg} appropriate to these complexes is about $4 \times 10^3\ \mathrm{cm^{-1}}$ and that the contribution from the solvent must be small. A small solvent reorganizational energy is plausible in view of: (a) the geometrical distance between metals in these complexes, 5.2 Å, is comparable to the mean effective radii of the donor and acceptor complex components, ~3 Å for ammine and ~6 Å for polypyridyl complexes, so $r \sim a$ (ave.) and $\chi_s \to 0$ (see Section 2.2); (b) and transition dipole length in these complexes appears to be smaller than the geometrical separation distance [31,68].

In the *cis* complexes, $[(bpy)_2Ru(CNRu(NH_3)_5)_2]^{3+}$ and $[(tpy)(bpy)Ru(CNRu(NH_3)_5)]^{4-}$, the Ru^{II}/Ru^{III} metal-to-metal charge transfer band (at 700 nm) has an absorptivity of 4.1×10^3 cm^{-1} M^{-1}/Ru^{III} [60], and H_{DA} has been estimated to be 3.5×10^3 cm^{-1} and $\varepsilon_s \cong 0.8 \times 10^3$ cm^{-1} [31]. The experimental values of $(h\nu_{max} - F\Delta E_{1/2})$ in water and Eq. (15) ($\alpha_N^2 \cong 0.06$) lead to a value of $\chi_{reorg} \cong 3.9 \times 10^3$ cm^{-1} for these systems in water. If this parameter is entirely attributed to the reorganizational free energy contribution of some low frequency vibrational modes, then the observed mean absorption bandwidth and Eq. (7) suggest a value of $\sigma \cong 0.7 \times 10^3$ cm^{-1}. A value of $\sigma \sim 700$ cm^{-1} has also been inferred from the vibronic bandwidths resolved in the 77 K MMCT emission (DMSO/H$_2$O glass) of *trans*-$[(NH_3)_5Cr(CNRu(NH_3)_5)]^{4+}$ [69]; the bandwidths should be a more direct measure of σ in frozen media (assuming that most of the low frequency reorganizational modes are frozen [36]). Unresolved electronic [31] or vibronic transitions could also contribute to the bandwidths in these complexes. If the value of χ_s were large compared to the high frequency vibrational quanta, then the band shapes could appear nearly gaussian and the vibronic structure could be literally washed out (as in Fig. 2b). That the quantity $\chi_r^* = (h\nu_{max} - F\Delta E_{1/2})$ and the absorption bandwidths are nearly independent of solvent and the size of the complexes would be consistent with such a contribution of unresolved components. This is illustrated by Eq. (7) with $\chi_h > \chi_l$ (see Fig. 2b). Any high frequency vibrational modes that give rise to an appropriate progression would have to be common to all these complexes. Very little distortion is expected in their metal–ligand bonds. This would probably require $h\nu_h < 10^3$ cm^{-1}; the $[(NH_3)_5Cr(CNRu(NH_3)_5)]^{4+}$ electron transfer emission at 77 K does seem to implicate a metal–nitrogen stretch ($h\nu \sim 400$ cm^{-1}) [39], but with a very small value of χ_h (thus a small distortion). Resonance Raman studies have implicated contributions of cyanide stretching frequencies to χ_{reorg} in some related, CN-bridged transition metal D/A complexes [70]. Thus, a progression in the CN stretch is a candidate for a contributing high frequency vibrational mode, but there is no clear marker of a progression in a 2000 cm^{-1} frequency. A progression in the CN stretch, analogous to the progression in Fig. 2b, would require $\chi_h > 3 \times 10^3$ cm^{-1} and $\chi_s \geq 2 \times 10^3$ cm^{-1}. Such parameters are not consistent with functions such as Eq. (7) or with the observed bandwidth. It should also be noted that the different excited state and ground state charge distributions very likely lead to different CN stretching force constants (based on the 25 cm^{-1} difference in the CN stretching frequencies of $[(bpy)_2Rh^{III}(CNRu^{II}(NH_3)_5)_2]^{5+}$ and $[(bpy)_2Ru^{II}(CNRh^{III}(NH_3)_5)_2]^{6+}$ [60,62]) and this would likely be another contribution to the bandwidth. These complexes demonstrate that a single, simple model does not readily describe all ‘simple’ electron transfer systems. A considerable amount of evidence has demonstrated that the CN-bridged donors and acceptors are vibronically coupled by the bridging ligand (i.e. H_{DA} is a function of the internal coordinates of CN) [31,39,60,61,63–67]. It may be necessary to consider this factor in order to adequately account for the apparent reorganizational energy (or bandwidth) behavior of these complexes.

4.3. Metal-to-ligand charge transfer in complexes with polypyridyl ligands

The ruthenium–polypyridine complexes form a nice comparison with the bimetallic complexes discussed in the preceding section since Ru^{II}/(polypyridine) and the $Ru^{II}/(CNRu^{III})$ absorptivities per chromophore are reasonably similar, while the transition dipole lengths are presumably different and give rise to significantly different electronic matrix elements; for example, H_{DA} has been inferred to be $\sim 10 \times 10^3$ cm^{-1} for the $(NH_3)_5Ru^{II}$/py metal-to-ligand charge transfer (MLCT) absorption from electroabsorption measurements [71] and $\sim 3.4 \times 10^3$ cm^{-1} $(tpy)(bpy)Ru^{II}/(CNRu^{III}(NH_3)_5)$ from electrochemical and spectroscopic studies [31]. The CT transition energies are 1.5–2 times larger for the MLCT transitions so the mixing coefficients, α_N, are also somewhat larger. In contrast to the relatively simple, single donor–single acceptor systems discussed above, the MLCT spectra of metal–(polypyridyl-ligand) complexes can be further complicated by: (a) the presence of two or more degenerate acceptor sites within the ligand (e.g. the two pyridine moieties of bpy); (b) mixing of nearly isoenergetic MLCT states that involve nominally independent ligands (e.g. in complexes with two or more polypyridyl ligands); and (c) possibly small energy differences between the LUMO and LUMO + 1 (these LUMOs of pyridine correlate with the degenerate components of the e_{2u} LUMO of benzene).

The symmetric and antisymmetric combinations of the coupled pyridine moieties in bipyridine complexes (point (a) above) typically lead to two MLCT transitions; this has been discussed in the literature [72,73]. If the lowest energy of these states is the symmetric combination, then Fig. 4 can qualitatively represent the MLCT

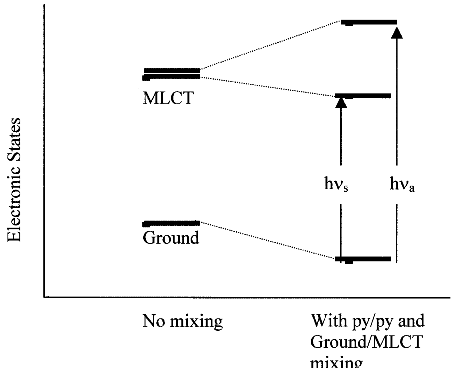

Fig. 4. A qualitative illustration of the mixing of the lowest energy metal-to-pyridine charge transfer states in a complex with a bipyridine ligand.

behavior of a mono-bipyridyl complex. Since electrochemical reduction of the ligand will access the lowest energy of these states, Eq. (16) is still appropriate.

The issue raised in point (b) above can become important when a complex contains two or more polypyridyl ligands. In such complexes, the one electron reduction of one ligand (electrochemically or in a MLCT excited state) results in what amounts to a mixed valence system (with respect to ligand valences) with the metal bridging the donor and acceptor ligands: (L)–M–(L^-). The extent of electronic coupling between the ligands in different oxidation states alters their energies by an amount ε_s(L), and this alteration affects the reduction of the remaining ligands (L). In acetonitrile, there are three distinct waves (in CV), separated by ~200 mV, in the electrochemical reductions of $Ru(bpy)_3^{2+}$ [74]. Similarly, the *first* bipyridine ligand reduction in acetonitrile of a series of $A_{6-2n}Ru^{II}(bpy)_n$ complexes (A an am(m)ine) occurs at increasingly negative potentials as n decreases (Table 3), also in increments of ~200 mV. Both observations could be the consequences of electronic coupling between the bipyridine rings, but the observations on $Ru(bpy)_3^{2+}$ are complicated by different electronic exchange, solvational (due to charge differences) and electrostatic repulsion contributions.

The coupling between the bipyridine ligands of $[Ru(bpy)_3]^{2+}$ at an extended Hückel level, analogous to the treatment of pyridine/pyridine mixing within the bpy ligand [72], by the secular determinant in Eq. (23)

$$\begin{vmatrix} -\varepsilon & H_{BB} & H_{BB} \\ H_{BB} & -\varepsilon & H_{BB} \\ H_{BB} & H_{BB} & -\varepsilon \end{vmatrix} = 0 \tag{23}$$

where H_{BB} is the matrix element representing coupling between ligands. This leads to two MLCT transitions (for each of the components mentioned at the beginning of this section) when H_{BB} is sufficiently large: $h\nu_1 = h\nu_2 = E^\circ_{MLCT} - H_{BB}$ and $\varepsilon_3 = E^\circ_{MLCT} + 2H_{BB}$. This would lead to a lowest energy MLCT transition in $[Ru(bpy)_3]^{2+}$ of about twice the intensity of that in $[(NH_3)_4Ru(bpy)]^{2+}$; the observation that ratio of intensities is about three to one suggests that H_{BB} is small. When H_{BB} is small, the electrochemical reductions of $[Ru(bpy)_3]^{2+}$ result in the transfer of an electron to a single ligand.

In the limit of the electrochemical reduction of one bipyridine ligand, one must take into account the vertical energy difference (the electron transfer reorganizational energy, λ_r) for moving the electron from one ring to another. This leads to Eq. (24) for the inter-ligand mixed valence problem (assuming that $H_{DA} \gg H_{BB}$), and to three non-degenerate solutions of the secular equation.

$$\begin{vmatrix} -\varepsilon & H_{DA} & H_{DA} \\ H_{DA} & \lambda_r - \varepsilon & 0 \\ H_{DA} & 0 & \lambda_r - \varepsilon \end{vmatrix} = 0 \tag{24}$$

Table 3
Charge transfer properties of some simple ruthenium bipyridine complexes

Complex	Solvent	$E_{1/2}(\mathrm{Ru^{III}} \mid \mathrm{Ru^{II}})$ (V)	$E_{1/2}(\mathrm{bpy} \mid \mathrm{bpy^-})$ (V)	$h\nu_{\max}$ ($\mathrm{cm^{-1}/10^3}$)		$F\Delta E_{1/2}$ ($\mathrm{cm^{-1}/10^3}$)	$h\nu_{\max} - F\Delta E_{1/2}$ ($\mathrm{cm^{-1}/10^3}$)
				I	II		
$[(bpy)_2Ru(bpy)]^{2+}$	CH_3CN	$+1.26 \pm 0.01$ [a]	-1.28 ± 0.03 [a]	22.17 [76–78]		20.5 ± 0.2	1.7
	H_2O	$+1.27 \pm 0.03$ [a]	-1.34 ± 0.04 [a]	22.12 [79–81]		21.1 ± 0.5	1.0
$[(phen)_2Ru(phen)]^{2+}$	CH_3CN	$+1.36 \pm 0.08$ [a]	-1.32 ± 0.11 [a]	22.62 [76]		21.7 ± 0.7	0.9
	H_2O	$+1.26$ [a]	-1.36 [a]	22.37 [78,79]		21.1 ± 0.2	1.3
$[(bpy)(en)Ru(bpy)]^{2+}$	CH_3CN	$+0.88$ [71]	-1.51 [71]			19.3	(1.2) [b]
	H_2O			20.53	28.99 [82]		
$[(bpy)(NH_3)_2Ru(bpy)]^{2+}$	CH_3CN	$+0.82$ [71]	-1.51 [71]			18	(1.6) [b]
	H_2O			20.41	28.99 [82]		
$[(en)_2Ru(bpy)]^{2+}$	CH_3CN	$+0.51$ [71]	-1.73 [71]			18.1	
	H_2O			19.42	27.4 [82]		(1.4) [b]
$[(NH_3)_4Ru(bpy)]^{2+}$	CH_3CN	$+0.55$ [40,82]	-1.67 [40,82]	19.08	27.47 [40,82]	17.9	1.2
$[(bpy)_2Ru(dpp)]^{2+}$	CH_3CN	$+1.40$ [40,83]	-1.06 [40,83]	21.26	22.76 [40,82]	19.84	1.5
$[(NH_3)_4Ru(dpp)]^{2+}$	CH_3CN	$+0.76$ [40]	-1.30 [40]	18.48	21.83 [40]	16.6	1.9
	H_2O	$+0.56$ [40]	-1.28 [40]	18.00	21.83 [40]	14.84	3.2

[a] Average of values listed in Ref. [84].

[b] $h\nu_{\max}(H_2O) - F\Delta E_{1/2}(CH_3CN)$.

This argument suggests that the first electrochemical reduction of $[Ru(bpy)_3]^{2+}$ will occur at $(FE^{\circ}_{1/2} - 2(H_{DA})^2/\lambda_r)$ in the limit that $\lambda_r > H_{DA}$ (the general solution is $\{E^{\circ}_{1/2} + [\lambda_r/2 - {}^1/_2(\lambda_r^2 + 8H_{DA}^2)^{1/2}]\}$). The related treatment of $[(NH_3)_2Ru(bpy)_2]^{2+}$ predicts that the first ligand reduction will occur at $E^{\circ}_{1/2} - (H_{DA})^2/\lambda_r$). For $[(NH_3)_4Ru(bpy)]^{2+}$ the first reduction would be at $E^{\circ}_{1/2}$, so that this argument, and the limit that $\lambda_r > H_{DA}$ are in good accord with the observations. After taking account of the statistical effect contributed by the different numbers of reducible rings in this series of complexes, assuming that λ_r and H_{DA} are the same in each complex and that no other factors contribute, then the experimental observations suggest that the stabilization energy conferred by each bipyridine–bipyridine interaction is ca. 0.06 eV. In a standard superexchange approach for bridge-mediated D/A coupling in a mixed valence system [8,75], the matrix element for bpy^-/bpy coupling in a (bpy^-)–Ru^{II}–(bpy) complex for which the matrix element for metal–ligand coupling is $H_{RuB} \sim 10 \times 10^3$ cm^{-1} (based on Ru^{II}/py coupling [71]) is given by Eq. (25).

$$H_{DA} \cong (H_{RuB})^2/2E_{RuB} \cong 2.3 \times 10^3 \text{ cm}^{-1} \tag{25}$$

If we set $\varepsilon \cong 480$ cm^{-1} (a value inferred above from the ligand electrochemistry), then this value of H_{DA} and the arguments presented above imply that $\lambda_r \cong 12 \times 10^3$ cm^{-1}. While the actual numerical values of all these parameters are certainly open to question, the argument does serve to emphasize the implications of the intense MLCT transitions of Ru^{II}/bpy complexes; there must be: (1) a great deal of metal–ligand mixing; (2) significant charge delocalization; (3) significant alteration of the properties of the metal and the ligand centers compared to those of unmixed systems; and (4) a Ru^{II} 'bridge' should be very effective in mediating the electron transfer coupling between bpy and bpy^- ligands. In contrast, the Ru^{III} center of the MLCT excited state should be much less effective in mediating the coupling between these ligands. Thus, the effective barrier, $\sim(\lambda_r/4 - H_{DA})$, for moving the electron from one bipyridine to another could be much greater in the MLCT excited state (e.g. of $[Ru(bpy)_3]^{2+}$) than in the one electron reduced polypyridyl complex (e.g. $[Ru(bpy^-)(bpy)_2]^+$). A greater concern in the context of this article is that the electrochemical data may contain a bpy^-/bpy stabilization energy contribution that is not relevant to the MLCT transition. If the above parameter estimates are reasonably valid, then the right hand side of equations such as (15) and (21) could underestimate $h\nu_{max}$ by about 10^3 cm^{-1}/bpy in a bis- or tris-bipyridine complex.

Some selected data for simple Ru^{II}–polypyridyl complexes are collected in Table 3 [40,76–84]. The apparent values of χ_{reorg} are small. The absorption band shapes of these complexes are more similar to Fig. 2a than to Fig. 2b or c, and this suggests that $\chi_l > \chi_h$ for them. The pertinent data in solvents other than acetonitrile are very limited.

We have noted that the large MLCT absorptivities imply significant attenuation of the reorganizational free energy contribution to $h\nu_{max}$. In order to illustrate this issue, we consider the $[Ru(NH_3)_4dpp]^{2+}$ complex and use $H_{DA} \cong 9 \times 10^3$ cm^{-1}

determined by Shin et al. [71] for $\mathrm{Ru^{II}}$/py coupling in $[\mathrm{Ru(NH_3)_5pz}]^{2+}$ as an approximation of H_{DA} in $\mathrm{Ru^{II}}$/dpp. This leads $\alpha_N \sim 0.49$ for the $\mathrm{(NH_3)_4Ru^{II}(dpp)}$ complex. This quantity can also be estimated using Eq. (15). If we take as an estimate of χ_r^{Ru} the value based on the $[\mathrm{Ru(NH_3)_4(bpy)}]^{3+,2+}$ self-exchange reaction (Table 1) and assume that the very rough estimate obtained above for $\chi_r^{bpy} \sim 12 \times 10^3$ cm^{-1} is also appropriate to the dpp ligand, then $\chi_{reorg}^{ex} = 11 \times 10^3$ cm^{-1}. Based on aqueous solution data in Table 3, $\chi_{reorg}^{*} \cong 3.2 \times 10^3$ cm^{-1}, and from Eq. (15) $(3.2 \times 10^3\ \mathrm{cm^{-1}}) \cong \chi_{reorg}^{ex}[1 - 4\alpha_N^2]$; $\alpha_N \sim 0.4$ and $\chi_{reorg}^{ex} \sim 9 \times 10^3$ cm^{-1} . The uncertainties in these estimates are very large, but their approximate agreement is reassuring. This example illustrates how strong D/A coupling tends to reduce reorganizational energies below values characteristic of the weak coupling limit. The somewhat greater solvent sensitivity of χ_{reorg}^{*} in the $[\mathrm{Ru(NH_3)_4dpp}]^{2+}$ system than inferred for the CN-bridged complexes of the preceding section is surprising in view of the much larger values of H_{DA} and α_N in the polypyridine complex. However, in each case χ_{reorg} is much smaller than in the related ion pair systems and the small solvent contribution for the $[\mathrm{Ru(NH_3)_4dpp}]^{2+}$ complex indicates appreciable attenuation of χ_s.

If the free energy contributions to the absorption maximum are based on electrochemical measurements, reorganizational free energies are expressed in terms of constituent self-exchange reaction reorganizational energies (χ_{reorg}^{ex}, Section 2.2) and if $\alpha_N > 0.45$, then the reorganizational contribution to the absorption maximum is approximately (Eq. (15)) $\chi_{reorg}^{ex}(1 - 4\alpha_N^2) < 0.2\chi_{reorg}^{ex}$. While the exact values of the parameters are not yet known, it is clear that the solvent reorganizational energy contributions to the MLCT absorption maxima are significantly attenuated in ruthenium^{II}–polypyridyl complexes. This is mostly a consequence of the significant amount of electron delocalization that results from metal–ligand mixing (i.e. $\alpha_N^2 > 0.1$). The electrochemical correlations with MLCT absorption energies should be particularly good in this type of system since cross terms, dependent on properties of both the donor and acceptor are expected to be relatively unimportant.

The 2,3-bis(pyridyl)pyrazine ligand exhibits some interesting contrasts with the 2,2′-bipyridine ligand. The HOMOs and LUMOs of the pendant pyridine moieties differ in energy from those of pyrazine (pz), so that configurational mixing between the rings is much weaker in dpp than in bpy and the lowest energy MLCT transitions are largely localized on the pz ring in the dpp complexes. Thus there are at least three $\mathrm{Ru^{II}}$/dpp MLCT transitions observed in $[\mathrm{(NH_3)_4Ru^{II}(dpp)}]^{2+}$, and the lowest two of these involve largely pz-centered LUMOs [40]. Ab initio calculations confirm that there is only a little energy difference between the LUMO and LUMO + 1 of dpp (these LUMOs correlate with the e_{2u} LUMO of benzene), and that the ordering of these orbitals is changed by minor perturbations such as the rotation of the pyridine rings with respect to the pyrazine ring [40]. The small quantitative differences may be related to the differences in LUMOs noted above, to differences in α_{DA} and/or to differences in χ_{reorg}.

5. Summary, problems and prospects

5.1. Summary

This article has considered the use of electrochemical and kinetic measurements on ground state species as a tool for investigating optical charge transfer transition in three types of systems: (a) ion pair charge transfer systems; (b) metal-to-metal charge transfer systems; and (c) metal-to-ligand charge transfer systems. The inter-relationship between the optical, the electrochemical and the kinetic electron transfer parameters is nicely illustrated by their correlation in ion pair systems. The ion pair systems constitute a limit in which the charge transfer absorption energy can be resolved into components that can be independently measured: the difference of the electrochemically determined free energies and one-half the sum of the reaction activation free energies (or the average of the reorganizational free energies, $\chi_{\mathrm{reorg}}^{\mathrm{ex}}$) of the constituent donor (D^+/D) and acceptor (A/A^-) electron transfer couples. Perturbation theory corrections of the constituent terms are generally small in this limit. D/A electronic coupling is much stronger in the Ru^{II}/polypyridyl complexes and optical/electrochemical correlations require correction of the constituent reorganizational free energy. This correction can be formulated in terms of a perturbation theory based attenuation of the constituent reorganizational free energy contributions. The strongly coupled Ru^{II}/bpy and $Ru^{II}/(CNRu^{III})$ complexes appear to lie at or near to a limit in which there is very little contribution of solvent reorganizational energy to the optical transition. One consequence of the relatively small reorganizational free energy contributions in strongly coupled systems is that the correlations of optical transition energies with electrochemical determinations of the free energy change that occurs when the donor is oxidized and the acceptor reduced should be relatively good since cross terms are expected to be small. However, this review has raised a concern that strong metal–ligand coupling may lead to a difference in the stabilization energy contributions in the optical and electrochemical measurements when contributions of several MLCT states are approximately degenerate.

5.2. Problems and prospects

In general, the optical absorption maximum can be represented, as in Eq. (26), as a sum of the individual contributions of the donor and the acceptor and a 'cross term' that depends on the properties of both.

$$h\nu_{\max} = F(\mathrm{D}) + F(\mathrm{A}) + f(\mathrm{D},\ \mathrm{A}) \tag{26}$$

The dominant individual contributions can usually be expressed in terms of donor and acceptor electrode potentials. In weakly coupled systems, $(H_{\mathrm{DA}}/E_{\mathrm{DA}}) < 0.1$, the electron transfer reorganizational energies of the constituent donor and acceptor electron transfer couples also contribute to $h\nu_{\max}$ in a simple, linear manner and cross terms are not a significant issue. However, the contributions of the constituent reorganizational energies are expected to diminish in proportion to the fraction of electron density delocalized, α_N^2. Since α_N^2, represented here as the ratio of the square of the electron transfer matrix element and the vertical energy difference between donor and acceptor, is intrinsically a function of both the donor and the acceptor, it cannot be easily factored into constituent components nor can it be easily transferred from one class of complexes to another. This is illustrated in the contrast of the behavior of complexes of the type $(X)_nRu^{II}(L)$ inwhich $(X)_n$ represents non-bridging (or 'bystander') ligands, Ru^{II} is the donor and the ligand L is the acceptor. In this report we focused on complexes in which L = 2,2′-bipyridine or in which $L = (CNRu^{III}(NH_3)_5)^{2+}$. For the former class of complexes, *f*(D,A) is solvent and donor dependent, and proportional to contributions of both the donor and the acceptor reorganizational parameters (reduced through the contributions of α_N^2). For the complexes with $(CNRu^{III}(NH_3)_5)^{2+}$ ligands, *f*(D,A) is approximately constant and nearly independent of solvent and donor properties. Clearly the contributions of the $(X)_nRu^{II}$ donor to *f*(D,A) that might be inferred from the $(X)_nRu^{II}(bpy)$ complexes cannot be transferred to the $[(X)_n,Ru^{II}(CNRu^{III}(NH_3)_5)]$ complexes. The contributions of cross terms to correlations become even greater when only variations in donor (or acceptor) electrode potentials are used.

The perturbation theory analysis employed here does indicate that careful comparisons of absorption maxima and donor–acceptor electrochemical and reorganizational energy data can provide some unique and useful perspectives on basic aspects of the charge transfer process.

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References

[1] R.S. Mulliken, W.B. Person, Molecular Complexes, Wiley-Interscience, New York, 1967.
[2] A.P.B. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[3] R.D. Cannon, Adv. Inorg. Chem. Radiochem. 21 (1979) 179.
[4] N.S. Hush, Electrochim. Acta 13 (1968) 1005.
[5] N.S. Hush, Prog. Inorg. Chem. 8 (1968) 391.
[6] J.F. Endicott, G.J. Ferraudi, J.R. Barber, J. Phys. Chem. 79 (1975) 630.
[7] S.I. Gorelsky, V.Y. Kotov, A.B.P. Lever, Inorg. Chem. 37 (1998) 4584.
[8] M.D. Newton, Chem. Rev. 91 (1991) 767.
[9] F. Salaymeth, S. Berhause, R. Yusof, R. de la Rosa, E.Y. Fung, R. Matamoros, K.W. Law, Q. Zhen, E.M. Kober, J.C. Curtis, Inorg. Chem. 32 (1993) 3895.
[10] D.E. Richardson, H. Taube, Coord. Chem. Rev. 60 (1984) 107.
[11] A.B.P. Lever, E. Dodsworth, in: E.I. Solomon, A.B.P. Lever (Eds.), Electronic Structure and Spectroscopy of Inorganic Compounds, Wiley, New York, 1999.
[12] N. Sutin, Adv. Chem. Phys. 106 (1999) 7.
[13] A.B.P. Lever, Inorg. Chem. 29 (1990) 1271.

[14] S. Lu, V.V. Strelets, M.F. Ryan, W.J. Pietro, A.B.P. Lever, Inorg. Chem. 35 (1996) 1031.
[15] A.B.P. Lever, Can. J. Anal. Sci. Spectrosc. 42 (1997) 22.
[16] S.I. Gorelsky, E.S. Dodsworth, A.B.P. Lever, A.A. Vlcek, Coord. Chem. Rev. 174 (1998) 469.
[17] R.A. Metcalfe, A.B.P. Lever, Inorg. Chem. 36 (1997) 4762.
[18] J.F. Endicott, in: V. Balzani (Ed.), Electron Transfer in Chemistry, vol. 1, Wiley/VCH, New York, NY, 2001, p. 238.
[19] T.J. Meyer, Progr. Inorg. Chem. 30 (1983) 389.
[20] J.C. Curtis, T.J. Meyer, Inorg. Chem. 21 (1982) 1562.
[21] J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, New York, 1970.
[22] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1985) 265.
[23] R.A. Marcus, Discuss. Faraday Soc. 29 (1960) 21.
[24] R.A. Marcus, Ann. Rev. Phys. Chem. 15 (1965) 155.
[25] N. Sutin, Progr. Inorg. Chem. 30 (1983) 441.
[26] C. Creutz, N. Sutin, Inorg. Chem. 15 (1976) 496.
[27] R.A. Marcus, J. Phys. Chem. 93 (1989) 3678.
[28] R. Englman, J. Jortner, Mol. Phys. 18 (1970) 145.
[29] N. Kestner, J. Logan, J. Jortner, J. Phys. Chem. 64 (1974) 2148.
[30] C.S.G. Phillips, R.J.P. Williams, Inorganic Chemistry, vol. I, Oxford University Press, New York, 1965.
[31] M.A. Watzky, A.V. Macatangay, R.A. Van Camp, S.E. Mazzetto, X. Song, J.F. Endicott, T. Buranda, J. Phys. Chem. 101 (1997) 8441.
[32] V.M. Kenkre, T.A. Tomakoff, M.D. Fayer, J. Chem. Phys. 101 (1994) 10 618.
[33] N.H. Damarauer, G. Cerullo, A. Yeh, T.R. Boussie, C.V. Shank, J.K. McCusker, Science 275 (1997) 54.
[34] N.H. Damarauer, J.K. McCusker, J. Phys. Chem. A 103 (1999) 8440.
[35] A.T. Yeh, C.V. Shank, J.K. McCusker, Science 289 (2000) 935.
[36] R.A. Marcus, J. Phys. Chem. 94 (1990) 4963.
[37] R.F. Loring, J. Phys. Chem. 94 (1990) 513.
[38] T.A. Rhodes, S. Farid, J.L. Goodman, I.R. Gould, R.H. Young, J. Am. Chem. Soc. 121 (1999) 5340.
[39] J.F. Endicott, P.G. McNamara, T. Buranda, A.V. Macatangay, Coord. Chem. Rev. 208 (2000) 61.
[40] D.S. Seneviratne, M.J. Uddin, V. Swayambunathan, H.B. Schlegel, J.F. Endicott, Inorg. Chem., submitted for publication.
[41] A. Myers, Acc. Chem. Res. 30 (1998) 519.
[42] I.R. Gould, D. Noukakis, G.-J. Luis, R.H. Young, J.L. Goodman, S. Farid, Chem. Phys. 176 (1993) 439.
[43] A. Haim, Comments Inorg. Chem. 4 (1984) 113.
[44] R. Billing, R. Benedix, H. Hennig, Z. Anorg. Allg. Chem. 600 (1991) 21.
[45] R. Billing, Coord. Chem. Rev. 159 (1997) 257.
[46] A. Vogler, A.H. Osman, H. Kunkley, Coord. Chem. Rev. 64 (1985) 159.
[47] T. Ramasami, J.F. Endicott, J. Am. Chem. Soc. 107 (1985) 389.
[48] R. Billing, D.E. Koshtariya, Inorg. Chem. 33 (1994) 4038.
[49] D.H. Macartney, Inorg. Chem. 30 (1991) 3337.
[50] A. Hammershoi, D. Geselowitz, H. Taube, Inorg. Chem. 23 (1984) 979.
[51] I. Creaser, R.J. Gene, J.M.B. Harrowfield, A.J. Herlt, A.M. Sargeson, M.R. Snow, J. Springborg, J. Am. Chem. Soc. 104 (1982) 6016.
[52] H.-J. Kueppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, Inorg. Chem. 25 (1986) 2400.
[53] D. Stanbury, Adv. Inorg. Chem. 33 (1987) 70.
[54] J.F. Endicott, T. Ramasami, D.C. Gaswick, R. Tamilarasan, M.J. Heeg, G.R. Brubaker, S.C. Pyke, J. Am. Chem. Soc. 105 (1983) 5301.
[55] J.F. Endicott, K. Kumar, T. Ramasami, F.P. Rotzinger, Prog. Inorg. Chem. 30 (1983) 141.
[56] G.M. Brown, N. Sutin, J. Am. Chem. Soc. 101 (1979) 883.
[57] F.P. Dwyer, A.M. Sargeson, J. Phys. Chem. 65 (1961) 1892.

[58] J.F. Endicott, G.R. Brubaker, T. Ramasami, K. Kumar, K. Dwarakanath, J. Cassel, D. Johnson, Inorg. Chem. 22 (1983) 3754.
[59] T.J. Meyer, H. Taube, Inorg. Chem. 7 (1968) 2369.
[60] M.A. Watzky, J.F. Endicott, X. Song, Y. Lei, A.V. Macatangay, Inorg. Chem. 35 (1996) 3463.
[61] A.V. Macatangay, X. Song, J.F. Endicott, J. Phys. Chem. 102 (1998) 7537.
[62] A.V. Macatangay, S.E. Mazzetto, J.F. Endicott, Inorg. Chem. 38 (1999) 5091.
[63] A.V. Macatangay, J.F. Endicott, Inorg. Chem. 39 (2000) 437.
[64] J.F. Endicott, X. Song, M.A. Watzky, T. Buranda, Chem. Phys. 176 (1993) 427.
[65] J.F. Endicott, X. Song, M.A. Watzky, T. Buranda, J. Photochem. Photobiol. A: Chem. 82 (1994) 181.
[66] J.F. Endicott, M.A. Watzky, A.V. Macatangay, S.E. Mazzetto, X. Song, T. Buranda, in: A.A. Kornyshev, M. Tosi, J. Ulstrup (Eds.), Electron and Ion Transfer in Condensed Media, World Scientific, Singapore, 1997, p. 139.
[67] J.F. Endicott, M.A. Watzky, X. Song, T. Buranda, Coord. Chem. Rev. 159 (1997) 295.
[68] L. Karki, H.P. Lu, J.T. Hupp, J. Phys. Chem. 100 (1996) 15 637.
[69] P.G. McNamara, A.V. Macatangay, J.F. Endicott, in preparation.
[70] K.S. Doorn, J.T. Hupp, J. Am. Chem. Soc. 111 (1989) 1142.
[71] Y.K. Shin, B.S. Brunschwig, C. Creutz, N. Sutin, J. Phys. Chem. 100 (1996) 8157.
[72] A.M. Zwickel, C. Creutz, Inorg. Chem. 10 (1971) 2395.
[73] W.L. Parker, G.A. Crosby, Int. J. Quantum Chem. 39 (1991) 299.
[74] G. Denti, S. Campagna, L. Sabatino, S. Seroni, M. Ciano, V. Balzani, Inorg. Chem. 29 (1990) 4750.
[75] C. Creutz, M.D. Newton, N. Sutin, J. Photochem. Photobiol. A: Chem. 82 (1994) 47.
[76] Y. Kawanishi, N. Kitamura, Y. Kim, S. Tazuke, Riken Q. 78 (1984) 212.
[77] A. Juris, V. Balzani, P. Belser, A. von Zelwesky, Helv. Chim. Acta 64 (1981) 2175.
[78] K. Nakamura, Bull. Chem. Soc. Jpn 108 (1986) 7872.
[79] C.T. Lin, M. Boettcher, M. Chou, C. Creutz, N. Sutin, J. Am. Chem. Soc. 98 (1976) 212.
[80] A. Harriman, J. Chem. Soc. Chem. Commun. (1977) 777.
[81] S.F. McClanahan, R.F. Dallinger, F.J. Holler, J.R. Kincaid, J. Am. Chem. Soc. 107 (1985) 4853.
[82] Y. Lei, PhD Dissertation, Wayne State University, 1989.
[83] R.W. Murphy Jr., K.J. Brewer, G. Gettliffe, J.D. Petersen, Inorg. Chem. 28 (1989) 81.
[84] A. Juris, F. Barigelletti, S. Compangna, V. Balzani, P. Belser, A. von Zelwesky, Coord. Chem. Rev. 84 (1988) 85.
[85] G.M. Brown, H.J. Krentzien, M. Abe, H. Taube, Inorg. Chem. 18 (1979) 3374.
[86] M.A. Watzky, PhD Dissertation, Wayne State University, Detroit, 1994.