

Some spectroscopic aspects of electron transfer in ruthenium(II) polypyridyl complexes

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Abstract—The metal-to-ligand charge transfer (MLCT) absorption and emission properties of several ruthenium(II)-bipyridine am(m)ine complexes are compared. The Gaussian deconvolution of the spectra indicates that: (a) the emission MLCT bandwidths are smaller than the absorption bandwidths for the first components of the apparent vibronic progressions; (b) the emission bands decrease in energy and width when a polypyridyl is replaced by an am(m)ine. The observations can be interpreted in terms of a two state model and the perturbation theory-based treatment of the attenuation of the effective reorganizational energy, $\lambda_r \cong \lambda_r^0(1 - 4\alpha_{DA}^2)$, where λ_r^0 is the reorganizational energy corresponding to no mixing between the two electron transfer states and $\alpha_{DA} = (H_{DA}/E_{DA})$ is the mixing coefficient. Both the solvent and molecular contributions to λ_r are attenuated. The MLCT excited state lifetimes also decrease with am(m)ine substitution, and the non-radiative decay rate constant at 77 K is roughly proportional to the number of am(m)ine moieties coordinated to the ruthenium center.

INTRODUCTION

Electron transfer is a ubiquitous, fundamental type of chemical reaction. Electron transfer reactions are important in all areas of chemistry and in applications as varied as the transduction of energy in biological systems and solar cells to the design of molecular level electronic devices [1]. Consequently, thermal electron transfer rates and optical electron transfer spectroscopy have been extensively studied and their general features are well understood [2–12]. However, there remain a number of poorly resolved, and often controversial areas. Among these are: (a) the effects of donor-acceptor electronic mixing on electron transfer processes; (b) the role(s) of bridging ligands in mediating electron transfer in covalently linked systems; (c) the role of high frequency modes in facilitating inverted region electron

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transfer; (d) whether there are selection rules for electron transfer processes. Most of these issues can be addressed in principle by combining thermal and optical measurements with perturbation theory based theoretical arguments for series of closely related compounds [4–7, 12–23].

Transition metal donor-acceptor systems have the advantage of a wide range of possible systems and of the relative ease of achieving systematic variations of critical parameters by means of changes in ligation, geometry, etc. It is a characteristic of these heavy metal complexes that several different electronic states can have very similar energies. This feature may be important in facilitating electron transfer and, thus, in the key role of transition metal complexes in biological electron transport systems. However, this proximity of electronic states leads to a great deal of configurational mixing and complicates many features of the electron transfer spectroscopy and the assignment of electron transport mechanisms of transition metal complexes. The spectroscopic complications include the convolution of the absorption envelopes for different electronic states, ambiguities of the assignment of the observed absorption (or emission) bands and a variety of perturbational effects that arise from the configurational mixings [13, 14, 24–27]. The effects of most relevance to this paper are of configurational mixing on the absorption and emission bandwidth and vibronic structure [4, 5, 11–14, 24–27]. Many of the parameters involved in these spectroscopic details are also important in determining the magnitude of thermal electron transfer rates [4, 5, 11, 12, 25, 26, 28–31]. In this paper, we summarize and review some recent studies of electron transfer absorption and emission and the non-radiative relaxation of electron transfer excited states in simple transition metal complexes.

SOME ISSUES RELATED TO THE ASSIGNMENT AND INTERPRETATION OF MLCT SPECTRA OF RUTHENIUM(II) POLYPYRIDYL COMPLEXES

The ruthenium polypyridyl complexes have been so much investigated [8, 32–37] that they are often used as a standard paradigm for the spectroscopy associated with the photoinduced transfer of an electron from a metal to an associated ligand (i.e. metal-to-ligand charge transfer, MLCT). The MLCT absorptions are typically broad for the complexes in ambient solutions, and they often exhibit absorption band asymmetries that are attributed to vibronic fine structure. These vibronic components can often be partially resolved in low temperature glasses. The dominant, high frequency vibronic components are generally believed to result from distortions of the 'reduced ligand' in the excited state. Thus, resonance Raman studies [38] have suggested that 83% of the molecular reorganizational energy associated with the lowest energy MLCT transition in $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$ derives from bipyridine centered distortions. Metal-ligand bond-lengths are generally very similar for Ru^{III} and Ru^{II} complexes, although the redistribution of charge in the MLCT excited state (e.g. the increased negative charge on the bpy ligand) may

result in metal-ligand bond length changes not commonly observed in the equivalent ground state species [38].

General features of MLCT absorption bands

In the simplest analysis, assuming a single coupled high frequency vibrational mode ($h\nu_h \geq 4k_B T$) and no overlapping bands, the MLCT absorption band can be described as [31]

$$\varepsilon(\nu_{abs}) = \frac{8N_A\pi^3}{3000h^2c\nu_{abs}} n^3 H_{DA}^2 \Delta\mu_{DA} FC, \quad (1)$$

$$FC = \sum_j F_{h,j} \exp\left[-(E_{DA}^{00} - h\nu_{abs} + jh\nu_h + \lambda_s)^2 / 4\lambda_s k_B T\right],$$

$$F_{h,j} = S_h^j [\exp(-S_h)] / [j!(4\pi\lambda_s k_B T)^{1/2}], \quad (2)$$

$$S_h = \lambda_h / h\nu_h,$$

where $\varepsilon(\nu_{abs})$ is the molar absorptivity at the frequency ν_{abs} , E_{DA}^{00} of the energy difference between the zeroth vibrational levels of the ground and excited state, $\lambda_{reorg} = (\lambda_h + \lambda_s)$ is the energy required to change the nuclear coordinates, within the molecule (λ_h) and in the solvent (λ_s), of the vibrationally equilibrated excited state (VEqES) into those of the ground state PE minimum. The vibrations that contribute to λ_h and λ_s are ν_h and ν_s ($h\nu_s \leq 4k_B T$), respectively. Equation (2) is written in terms of the sum over the quantum levels ($j = 0, 1, 2, \dots$) of a single high frequency vibrational mode ($h; \nu_h \gg k_B T/h$) for simplicity, but several high frequency modes contribute to the excited state distortion of most molecules. Equation (2) leads to a Gaussian band-shape with a maximum given by

$$h\nu_{\max}(\text{abs}) \cong E_{DA}^{00} + \lambda_s + \dots, \quad (3)$$

when the high frequency vibronic structure is either resolved or unimportant. The vibronic contributions, $jh\nu_h$, correspond [in the context of equations (1) and (2)] to a series of Gaussian peaks, each with a full width at half height of [4, 5, 18],

$$\Delta\nu_{1/2} = 4(k_B T \lambda_s \ln 2)^{1/2}, \quad (4)$$

and maxima at,

$$h\nu_{\max}(\text{abs}) \cong E_{DA}^{00} + \lambda_s + jh\nu_h, \quad j = 0, 1, 2, \dots \quad (5)$$

When λ_s is large enough that the vibronic structure is convoluted into the absorption band envelope, then the band may be asymmetric and λ_h may contribute to the effective value of $\Delta\nu_{1/2}$.

Absorptions of Ru^{II}-bipyridine complexes

Equations (1) and (2) form the basis for a Gaussian analysis of MLCT absorptions, but caution must be exercised in using them to fit Ru^{II}/polypyridyl MLCT spectra since: (a) even complexes with a single bipyridine ligand, such as [Ru(NH₃)₄bpy]²⁺, exhibit more than one resolved MLCT band [8, 39, 40]; (b) resonance Raman studies of the lowest energy, resolved MLCT bands of Ru^{II} bipyridyl complexes indicate that several high frequency vibrational modes are coupled to them [38]; this would require a sum over the different ν_h contributions in Equation (1); (c) even the intense, ambient MLCT ‘bands’ appear to be the convolution of more than one electronic contribution [27, 41]. In view of this, any attempt to fit the observed spectrum of [Ru(NH₃)₄bpy]²⁺ to the single mode expression, equation (1), may be misleading even if the parameter fitted as ν_h is interpreted as an ‘averaged’ high frequency mode. It is more appropriate to use equation (1) as the basis for the Gaussian deconvolution of the observed spectrum. Even then one should not force all the Gaussian components to have the same bandwidth since: (a) the components in such a resolved spectrum are likely to be the convolution of several high frequency modes whose frequency differences are small compared to their bandwidths; and (b) some of the higher energy components may be weak electronic rather than vibronic components. While the absorption spectra of complexes with a single polypyridine ligand have been found to be complicated, as noted here and discussed further below, detailed spectral analyses of these complexes are possible. On the other hand, inter-chromophore mixing is bound to make the spectral analysis of complexes with several polypyridyl ligands, such as [Ru(bpy)₃]²⁺, much more complicated, and we are not aware of any detailed analysis to date that properly accounts for the resulting problems.

The spectral assignment of even the most intense and resolved MLCT absorption bands of polypyridine complexes has been somewhat complicated. In order to gain some insight into the issues involved, we have carried out computations on the bpy ligand with the Gaussian series of programs [42]. The bpy ligand was constrained to a planar geometry and fully optimized at the HF/LANL2DZ level of theory. This consists of the Los Alamos pseudopotentials on heavy atoms and the D95V all electron basis on first and second period atoms.

In making the assignments, we employ the usual ligand-field-type of assumption that the metal and ligand electronic structures are only perturbationally altered by the formation of metal-ligand bonds [43]. That the metal-ligand mixing does not dramatically change the nature of either component in these complexes has been demonstrated by the successes of the numerous simple resolutions of their molecular properties into the sum of metal properties plus ligand properties, with only a small perturbational correction term to accommodate the changes in properties that result from the interaction of the donor and acceptor [9, 44–48]. The correction term is often formulated in terms of the fraction of electron density delocalized between the donor and the acceptor. A measure of this is the normalized, squared mixing coefficient, $\alpha_{DA}^2 = (H_{DA}/E_{DA})^2$. For the Ru^{II}/bpy complexes that

are the focus of this paper, α_{DA}^2 has been estimated to less than about 10% in their ground states [27, 49, 50]. Of course, some molecular properties are very sensitive to variations in α_{DA}^2 . Notable among these are the absorption (or emission) band intensity and width [4, 5, 18, 25, 26]. One expects that the band shape (or vibronic structure) should also vary with α_{DA}^2 .

The general sources of the difficulties in making spectroscopic assignments are a consequence of the electronic structures of the component ligand and metal. For example, the LUMO and LUMO + 1 of pyridine are not greatly different in energy, they correlate with the e_{2u} LUMO of benzene, and both must be considered in the spectral assignments. Furthermore, there are three $d\pi$ orbitals at Ru^{II} , de-

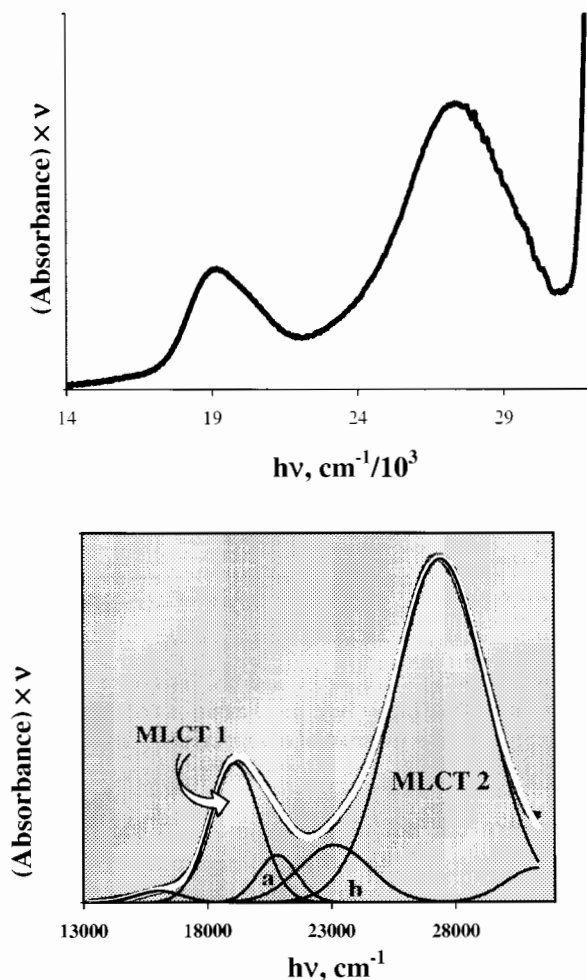


Figure 1. MLCT absorption spectra of $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$. Upper spectrum, experimental spectrum (scaled absorbance); lower spectrum, results of Gaussian deconvolution (heavy black line is the experimental spectrum, white line is the sum of the Gaussian components, Gaussian components are the black lines).

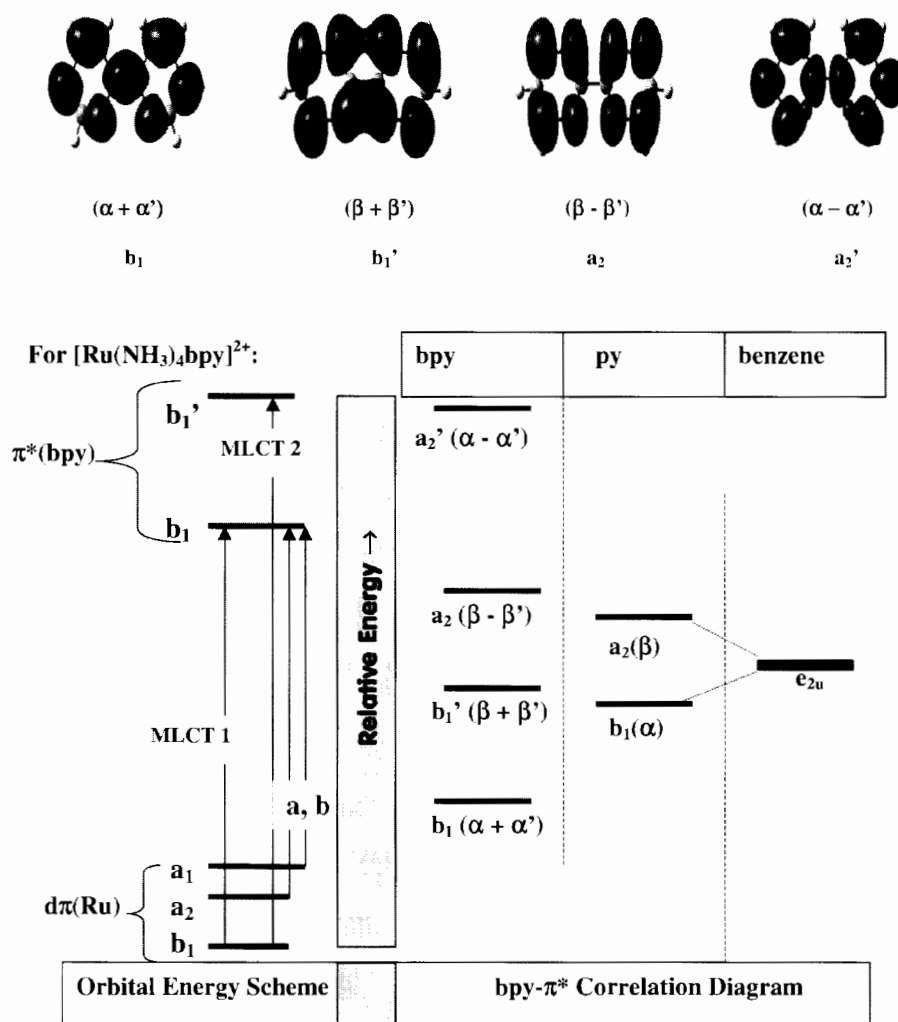


Figure 2. Summary of *ab initio* calculations and the assignment of MLCT transitions in $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$: top, π^* orbitals of planar bpy; rhs, diagram correlating the π^* orbitals of benzene, pyridine and planar 2,2'-bipyridine; lhs, assignment of lowest energy transitions in $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$.

generate in O_h symmetry but not non-degenerate in the polypyridyl complexes, and these may all contribute to the observed absorptions in low symmetry complexes. Thus, in ambient solutions $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$ exhibits two well resolved, non-Gaussian [in the sense of equations (1) and (2)] MLCT absorption band envelopes (Fig. 1). The origin of the two most intense components has traditionally been attributed to transitions that involve the symmetric and antisymmetric combinations of component pyridine LUMOs [39, 40]. However, *ab initio* calculations on the free, planar bipyridine ligand indicate that while the LUMO can be regarded as the 'symmetric' combination (b_1 in C_{2v}) of pyridine LUMOs, the LUMO + 1 of

bpy also has b_1 symmetry and is better interpreted as the 'symmetric' combination of pyridine LUMO + 1s [14, 27]. Both the LUMO and LUMO + 1 of bpy have large orbital coefficients at the nitrogens and would be expected to overlap strongly with the $d\pi$ (b_1) orbital of Ru^{II} , leading to intense absorptions; see Fig. 2.

The spectroscopic consequences that result from the LUMO/LUMO + 1 mixings of the aromatic ring components of polypyridyl ligands are an even greater problem when different types of rings are combined. Notable examples of this can be found among the pyridine substituted pyrazine ligands. Thus, the LUMO of 2,3-(2-pyridyl)pyrazine (dpp), configured to coordinate one or two metals, is correlated with the LUMO + 1 of pyrazine [27]. This computational result is easily interpreted to be the result of stronger mixing between the LUMOs of the pyridine substituents and LUMO + 1 of the pyrazine than with the pyrazine LUMO. As a consequence the orbital coefficients on the nitrogens of the pyrazine moiety of the dpp LUMO differ in their relative phase from those of the pyrazine LUMO, and this appears to limit the contributions of the dpp LUMO to metal-metal mixing in dpp-bridged complexes [27]. This assignment accounts for some spectroscopic features of complexes with dpp ligands. Thus, the second (or higher energy), dominant MLCT component of $[Ru(NH_3)_4dpp]^{2+}$, assigned as a transition involving LUMO + 1, does not appear as a resolved band in the spectrum of $[Ru(NH_3)_4]_2dpp^{4+}$, but the lowest energy MLCT transition has about twice the intensity (per Ru) in the bimetallic as in the monometallic complex. This is consistent with a Jahn-Teller splitting of the second MLCT transition (involving LUMO + 1) and the convolution of its lowest energy component with the lowest energy MLCT transition (involving the dpp LUMO). The magnitude of the proposed splitting of the upper MLCT excited state, formally a mixed valence species $[Ru^{II}(NH_3)_4(dpp^-)Ru^{III}(NH_3)_4]^{4+}$, is similar to the energy of the Ru^{II}/Ru^{III} MMCT absorption band of the ground state of the $[Ru^{II}(NH_3)_4(dpp)Ru^{III}(NH_3)_4]^{5+}$ mixed-valence complex [27, 51].

Electron transfer emissions of Ru^{II} -bipyridine complexes

Many, if not most of the MLCT excited states of ruthenium-polypyridyl complexes exhibit intense, nominally phosphorescence emissions, and these have been very extensively studied [52]. The focus here will be on some aspects of the emission spectroscopy of these complexes that appear to have received relatively little attention: (a) the variations of emission band shape with emission energy; (b) estimates of the singlet-triplet energy differences and variations of the exchange energy among the complexes. Our approach to these issues is based on the Gaussian deconvolution of the emission spectra. Since some of the vibronic structure is resolved in low temperature glasses, we have also examined the attenuation of λ_n with increasing delocalization of electron density.

Bandwidths and bandshapes of electron transfer absorptions and emissions.

The bandwidth of an electron transfer absorption is expected to decrease with increasing delocalization of charge between the donor and acceptor [4, 5, 14, 24–27].

The configurational mixing between the ground and electron transfer excited states results in a decrease of the separation of their potential energy minima by an amount $2(\alpha_{\text{DA}}^2 + \alpha_{\text{AD}}^2)x_0$, where x_0 represents the difference in the nuclear coordinates of the PE minima before any configurational mixing and α_{DA} and α_{AD} are the mixing coefficients at the ground state and excited state PE minima, respectively. This leads to a modification of equation (4) [26],

$$\Delta\nu_{1/2} \cong 4[k_{\text{B}}T\lambda_{\text{s}}^0(1 - 4\alpha_{\text{DA}}^2)]^{1/2}, \quad (6)$$

where λ_{s}^0 is the solvent reorganizational energy in the limit that $\alpha_{\text{DA}}^2 = 0$. It is to be noted that the effective reorganizational energy, $\lambda_{\text{s}} = \lambda_{\text{s}}^0(1 - 4\alpha_{\text{DA}}^2)$, is expected to be very strongly attenuated by delocalized charge in any system with an intense electron transfer absorption since the absorptivity varies in proportion to α_{DA}^2 [31]. In order to fully utilize equation (1) it is necessary to have some means of evaluating λ_{s}^0 . We have been exploring the use of thermal, electron transfer kinetic data for this purpose [13, 14, 24, 27] since [2–6, 12, 53],

$$k_{\text{exch}} \cong K_0\kappa_{\text{el}}\nu_{\text{eff}}e^{-(\lambda_{\text{s}}^0/4k_{\text{B}}T)}, \quad (7)$$

where k_{exch} is the rate constant for bimolecular self-exchange electron transfer,



K_0 is an ion-pair association constant, κ_{el} (the electronic transmission coefficient) is assumed to be close to one and ν_{eff} is the effective nuclear vibrational frequency at the transition state. Values of λ_{s}^0 , tabulated elsewhere [13, 14], have been extracted from experimental kinetic data for self-exchange electron transfer reactions and shown to correlate nicely with observed ion pair electron transfer (IPCT) absorption band energies [13, 14]. Since the IPCT absorptions tend to be weak (absorptivities less than $10^3 \text{ M}^{-1} \text{ cm}^{-1}$), these reorganizational parameters are plausible estimates of λ_{s}^0 .

Because mixing is presumed to be large in the systems considered here, we have considered the higher order terms that might modify equation (6). For x_0 the separation of ground state and excited state PE minima (in the correlated nuclear coordinate), H_{DA} the coupling matrix element (assumed to be coordinate independent), E_{DA}^{00} the energy difference of the two PE minima, $\varepsilon_{\text{DA}}^0 = [H_{\text{DA}}^2/(E_{\text{DA}}^{00} + \lambda_{\text{r}}^0)]$ and k a force constant. The adiabatic excited state (V^+) and ground state (V^-) surfaces, evaluated in the coordinate x , are most simply represented as,

$$\begin{aligned} V^+(x) &= E_{\text{DA}}^{00} + 1/2k(x_0 - x)^2 + \varepsilon_{\text{s}}(x) \\ &= E_{\text{DA}}^{00} + 1/2k(x_0 - x)^2 + H_{\text{DA}}^2/[E_{\text{DA}}^{00} + \lambda_0 - kx_0x] \\ &\cong E_{\text{DA}}^{00} + \lambda_0 - kx_0x + 1/2kx^2 + \varepsilon_{\text{DA}}^0(1 + kx_0x/E_{\text{DA}}^0), \end{aligned} \quad (9)$$

$$\begin{aligned} V^-(x) &= 1/2k(x)^2 - H_{\text{DA}}^2/[E_{\text{DA}}^{00} + \lambda_0 - kx_0x] \\ &\cong 1/2kx^2 - \varepsilon_{\text{DA}}^0(1 + kx_0x/E_{\text{DA}}^0). \end{aligned} \quad (10)$$

The reorganizational energy appropriate to the absorption, the vertical transition from the adiabatic ground state, is given by $\Delta V_a^+ = [V^+(\alpha_{DA}^2 x_0) - V^+(x_0 - \alpha_{AD}^2 x_0)]$, or,

$$\Delta V_a^+ = \lambda_r^0 [1 - 4\alpha_{DA}^2 + \alpha_{DA}^4 (3 + 2z^2 - z^4)] = \lambda_r(\text{absorption}), \quad (11)$$

where $\alpha_{AD} = z\alpha_{DA}$ and $z = (E_{DA}^{00} + \lambda_{\text{reorg}}^0)/(E_{DA}^{00} - \lambda_{\text{reorg}}^0)$.

Similarly, for the emission (parameters defined with respect to the excited state PE minimum, $x = (1 - \alpha_{AD}^2)x_0$ with $y = (\alpha_{AD}/\alpha_{DA}) \geq 1.0$),

$$\Delta V_f^- = \lambda_r^0 [1 - 2\alpha_{AD}^2 (1 + y^2) + \alpha_{AD}^4 (1 + 2y^2 + y^4)] = \lambda_r(\text{emission}). \quad (12)$$

Since $\varepsilon_{AD} > \varepsilon_{DA}$ when $E_{DA}^{00} > 0$, the emission bandwidth is expected to be smaller than the absorption bandwidth (Fig. 3a), and the dominant Gaussian components of our deconvoluted spectra are consistent with this expectation. These equations predict different variations of the absorption and emission bandwidths with solvent reorganizational energy, or more correctly, with the ratio of λ_r^0 to E_{DA}^{00} ; an example of this is shown in Fig. 3b. The bandwidth arguments presented here represent an idealized limit in which λ_r^0 and E_{DA}^{00} are unique quantities with identical values for all molecules in solution and probed by the measurement. This is not likely to be the case in solution since there is inevitably a distribution of molecular solvent environments and both λ_r^0 and E_{DA}^{00} vary with solvent environment. If this effect is important, it requires the addition of a term, σ (the deviation from the mean value of $[E_{DA}^{00} + \lambda_r]$), to equations (4) and (6) [13, 14, 54].

Most of the deconvoluted bandwidths are smaller for emission than for absorption in the same complex, the opposite order is found for $[\text{Ru}(\text{bpy})_3]^{2+}$: In ambient DMSO/H₂O solutions $\Delta\nu_{1/2} = 1990$ and 1880 cm^{-1} , respectively, for the dominant (high and low energy, respectively) MLCT components. Equations (6), (10) and (11) predict that the bandwidth should be 2–5% larger for absorption than for emission. A very simple interpretation of this contradiction is that the electrons are more delocalized in the Franck-Condon excited state than in the emitting state. This interpretation is consistent with appreciable bpy/bpy coupling and the concomitant delocalization of electron density between the ligands.

The behavior of the other complexes that we have examined is much more consistent with expectation. For example, the ambient emission and absorption bandwidths of $[\text{Ru}(\text{NH}_3)_2(\text{bpy})_2]^{2+}$ are 1820 and 2120 cm^{-1} , respectively. The ratio of these bandwidths suggests that $\alpha_{AD}^2 \cong 0.11$ and $\alpha_{DA}^2 \cong 0.05$ for this complex (assuming that $y \cong h\nu_{\text{max}}(\text{emis.})/h\nu_{\text{max}}(\text{abs.})$). It is important to note that the observed bandwidths are much smaller than would be the case if no electron density were delocalized. Thus, the solvent reorganizational contribution for the donor alone should contribute between 2200 and 4400 cm^{-1} to λ_r^0 for these complexes (based on electron transfer kinetic data [13, 14, 27]). The far smaller observed values of λ_r imply that there is appreciable attenuation of the bandwidth due to electron delocalization in these complexes; our previous estimates were $\alpha_{DA}^2 \approx 0.06$ – 0.09 for the three Ru^{II}/bpy complexes considered here [27]. Despite this considerable

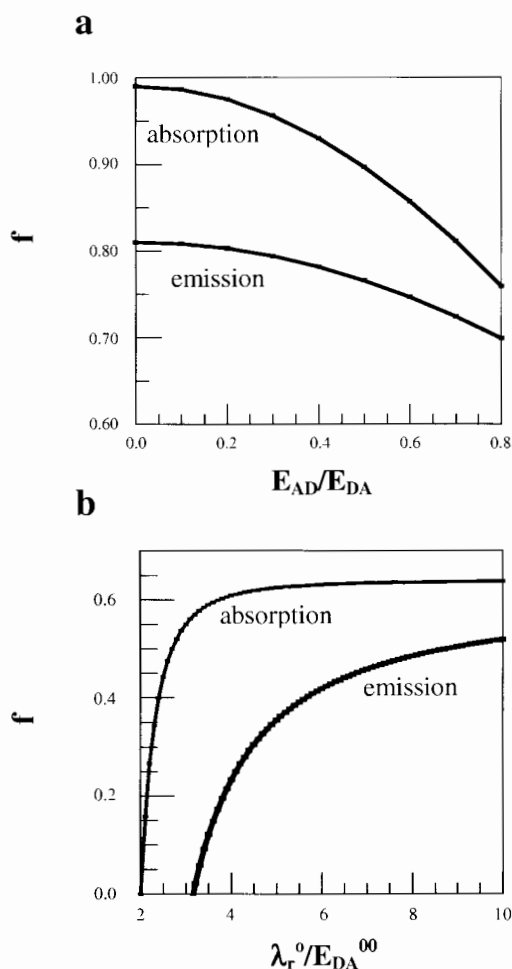


Figure 3. Variations of the attenuation factor, $f = \lambda_r/\lambda_r^0$ (equation (11) for absorption; equation (12) for emission) with the ratio of emission to absorption energy (top) and with the ratio of the limiting reorganizational energy, λ_r^0 , to E_{DA} . Calculations based on $\alpha_{DA}^2 = 0.1$.

attenuation, the bandwidths are significantly larger in the DMSO/H₂O solvent than in butyronitrile as expected for the stronger solvation of the former.

Photoacoustic and thermal lensing calorimetries have been used to make relatively direct estimates of the ³MLCT energy of [Ru(bpy)₃]²⁺ [55, 56]. Based on measurements in ambient aqueous solutions, $E_{DA}^{00}(\text{}^3\text{MLCT}) = (16.8 \pm 0.6) \times 10^3 \text{ cm}^{-1}$. This is smaller than the sum $h\nu_{\text{max}}(\text{emis})$ and $\lambda_r(\text{emis})$ (from Table 1: $[16.20 + 1.6] \times 10^3 \text{ cm}^{-1} = 17.8 \times 10^3 \text{ cm}^{-1}$; note that the use of parameters from the deconvoluted spectra implies that $\lambda_r = \lambda_s$) by about 1000 cm^{-1} . Unfortunately, the accumulated uncertainties ($\sim \pm 900 \text{ cm}^{-1}$) are comparable to this difference, but the comparison does suggest that $\sigma > 0$. In the analysis here, we assume that σ is negligibly small (the simplest assumption), so our values of λ_r should be consid-

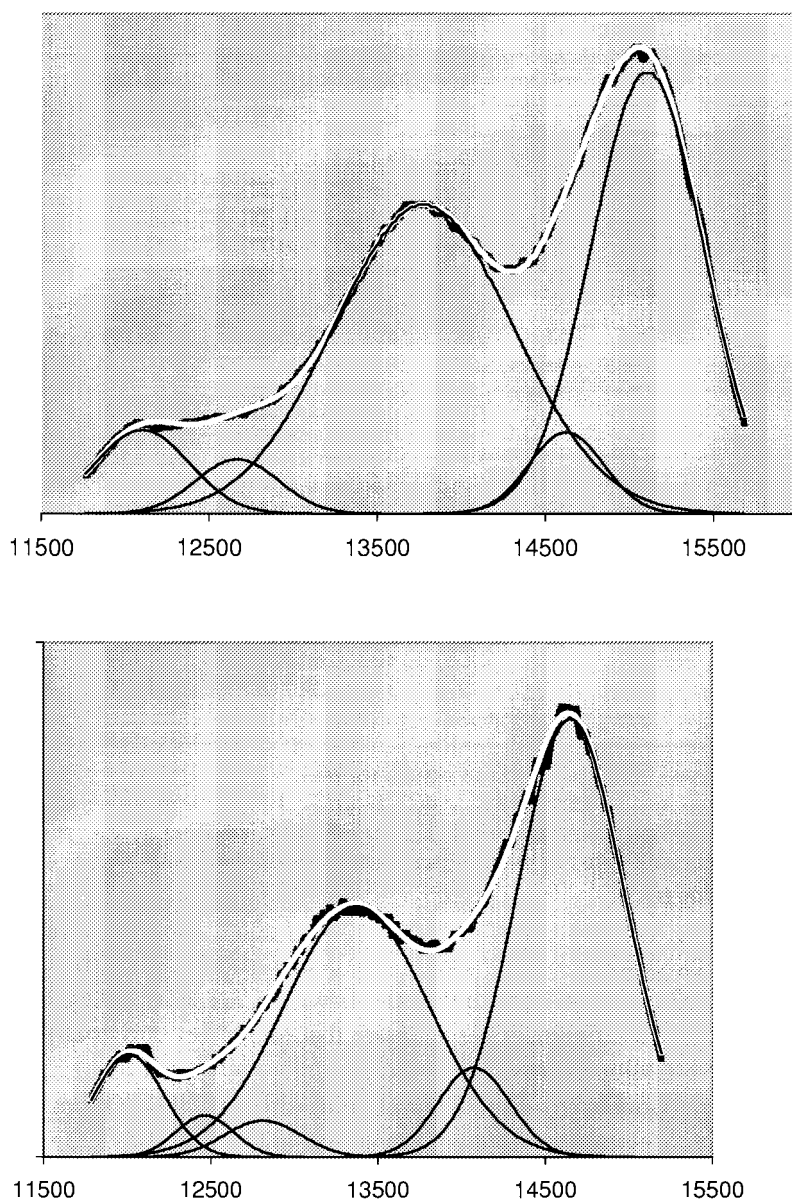


Figure 4. Comparison of the Gaussian deconvolution of the emission spectra of $[\text{Ru}(\text{bpy})_3]^{2+}$, top spectrum, and $[\text{Ru}(\text{NH}_3)_2(\text{bpy})_2]^{2+}$, bottom spectrum; in butyronitrile glass at 77 K. The two spectra have the same energy scale. Heavy black curves are the experimental spectra and the white curves are the sum of Gaussian components.

ered to be upper limits. One additional issue should be considered in evaluating the difference between the photoacoustic/thermal lensing and spectroscopic estimates of E_{DA}^{00} ($^3\text{MLCT}$): spin-orbit coupling in this complex is known to split the $^3\text{MLCT}$ state into components, and the higher energy components have the largest emission

Table 1.

Complex	<i>T</i> (K)	Solvent	$h\nu_{\max}(\text{emis.})^a$ ($I_{\max}/I_{\max}^{\text{ref}}$) [$\Delta\nu_{1/2}$]	$h\nu_{\max}(\text{abs})^a$ [$\Delta\nu_{1/2}$]	$\lambda_s(\text{emis.})^{a,b}$ [λ_h]	
[Ru(bpy) ₃] ²⁺	77	DMSO/H ₂ O	17.12 (1.0) [0.78]	21.84 [1.88]	1.03 [1.1]	
			15.9 (0.89) [1.22]			
			14.5 (0.38) [1.35]			
	77	<i>n</i> -butyronitrile	17.34 (1.0) [0.72]		0.88 [1.1]	
			15.9 (0.88) [1.10]			
			14.6 (0.34) [1.26]			
298	DMSO/H ₂ O	16.20 [1.9]	21.84 [1.88]	1.6		
		16.46 [1.4]				
[Ru(en)(bpy) ₂] ²⁺	77	DMSO/H ₂ O	14.97 (1.0) [0.81]	20.4	1.11 [0.9]	
			13.7 (0.67) [1.23]			
	77	<i>n</i> -butyronitrile	15.11 (1.0) [0.79]		20.4	1.06 [0.9]
			13.8 (0.70) [1.26]			
	298	DMSO/H ₂ O	14.18 [1.8]		20.4	1.4
			14.58 [1.55]			
[Ru(NH ₃) ₂ (bpy) ₂] ²⁺	77	DMSO/H ₂ O	14.61 (1.0) [0.85]	20.41 [2.1]	1.22 [0.8]	
			13.47 (0.68) [1.10]			
	77	<i>n</i> -butyronitrile	14.66 (1.0) [0.75]		20.41 [2.1]	0.95 [0.7]
			13.38 (0.6) [1.00]			
	298	DMSO/H ₂ O	13.78 [1.8]		20.41 [2.1]	1.4
			14.38 [1.55]			
298	<i>n</i> -butyronitrile	14.38 [1.55]	20.41 [2.1]	1.05		
		14.38 [1.55]				

^a All energies in cm⁻¹/10³; solutions of complexes in 1:1 (v:v) DMSO/H₂O; peak maxima and bandwidths from spectra deconvoluted using Grams/32 if both quantities are entered; if only the energy of the band maximum is entered, it is based on the emission or absorption envelope; $I_{\max}/I_{\max}^{\text{ref}}$ = intensity relative to that of the highest energy major component.

^b Based on equation (4).

efficiencies [32, 37]. This will make the sum ($h\nu_{\max} + \lambda_r$) > E_{DA}^{00} , and it accounts for a small part of the difference; we estimate that this effect will contribute about 200 cm⁻¹ to the emission energy.

The emission maxima in frozen solution are blue-shifted (200–900 cm⁻¹) relative to those in ambient solutions. The shifts are largest in DMSO/H₂O. One interpretation of these shifts is that some of the solvent reorganizational modes are frozen at 77 K [57]. For the frozen solvent modes designated by $\delta\lambda_s$ and the ambient PE minimum by E_{DA}^{00} , the excited state in a rigid medium should have its PE minimum at $E_{\text{DA}}^s = (E_{\text{DA}}^{00} + \delta\lambda_s)$. The bandwidth differences and the differences in estimates of λ_s [from equation (6)] are too small to account for these shifts in emission maxima.

Overall, the bandwidths observed for MLCT transitions in Ru(II)-polypyridyl complexes are appreciably narrowed relative to their estimated values in the absence of charge delocalization. General features of the MLCT spectra, such as the variations in transition energy and absorption and emission bandwidths, follow expectation based on simple perturbation theory approaches.

Singlet–triplet energy differences and the exchange energy (K_{exch}) contributions

The singlet-triplet energy difference is approximately given by,

$$E_{\text{ST}} \cong h\nu_{\text{max}}(\text{abs}) - h\nu_{\text{max}}(\text{emis.}) - [\lambda_{\text{r}}(\text{abs}) + \lambda_{\text{r}}(\text{emis.})] = 2K_{\text{exch}}, \quad (13)$$

where $\lambda_{\text{r}} = \lambda_{\text{s}}$ for the components in the resolved spectra. Values of the transition energies and λ_{s} can be obtained as described above. The observations summarized in Table 1 for ambient DMSO/H₂O solutions can be used to estimate E_{ST} . For $[\text{Ru}(\text{NH}_3)_2(\text{bpy})_2]^{2+}$, $\Delta h\nu_{\text{max}} = 6640 \text{ cm}^{-1}$, $\lambda_{\text{s}}(\text{emis.}) \cong 1400 \text{ cm}^{-1}$, $\lambda_{\text{s}}(\text{abs}) \cong 1930 \text{ cm}^{-1}$ and $E_{\text{ST}} \cong 3.3 \times 10^3 \text{ cm}^{-1}$. The uncertainty in this estimate, the difference between large numbers, is appreciable. If we take account only of the uncertainty in the bandwidth estimates (about 10%), then E_{ST} would have an uncertainty of about $\pm 500 \text{ cm}^{-1}$. The anomalously narrow absorption bandwidth for $[\text{Ru}(\text{bpy})_3]^{2+}$ has been noted above. If we assume that a more appropriate absorption bandwidth is about 15% larger than the emission bandwidth, then $\lambda_{\text{s}}(\text{abs}) \sim 1.3\lambda_{\text{s}}(\text{emis.})$ and $E_{\text{ST}} \sim 2.5 \times 10^3 \text{ cm}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$. Uncertainties about the effects of configurational mixing with higher energy states (such as inter-ligand CT states) and the distribution of solvation environments make it very difficult to evaluate the significance of this estimate. Lever and Gorelsky have used ZINDO methods to calculate $2K_{\text{exch}} \cong E_{\text{ST}} = 4160$ and 1460 cm^{-1} for $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$, respectively [49]. The calculated values are comparable to our estimates for $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$ (and smaller for $[\text{Ru}(\text{bpy})_3]^{2+}$, but the significance of the difference is not clear) based on experimental observations, and with K_{exch} increased by each replacement of bpy by two NH₃.

Vibronic structure

In principle, the resolved vibronic components are a measure of λ_{h} and $h\nu_{\text{h}}$ (based on the emission analog of equation (2)). Thus the ratio of the intensity of the first vibronic component ($j = 1$) of the intensity of the band origin ($j = 0$) is equal to $S_{\text{h}} = \lambda_{\text{h}}/h\nu_{\text{h}}$ [31, 58]; the energy difference between these components should be equal to $h\nu_{\text{h}}$. The complexes considered here exhibit two to four emission band components which are reasonably well resolved at 77 K. These have been assigned as vibronic components. These ‘vibronic components’ appear to be the superposition of several components [38], and their bandwidths are significantly different. The second highest energy component in each complex has its emission maximum (1300 ± 200) cm^{-1} lower in energy than the dominant component. Since several bpy-centered vibrations appear to contribute to the intensity in the 1100–1600 cm^{-1} range [38], we interpret the 1300 cm^{-1} component as an ‘average’ or composite of these bpy vibrations. The relative intensity of this component decreases with the energy of the emission band, in accord with expectation for attenuation of the high frequency vibrational reorganizational contributions,

$$\lambda_{\text{h}} \cong \lambda_{\text{h}}^0(1 - 4\alpha_{\text{LD}}^2). \quad (14)$$

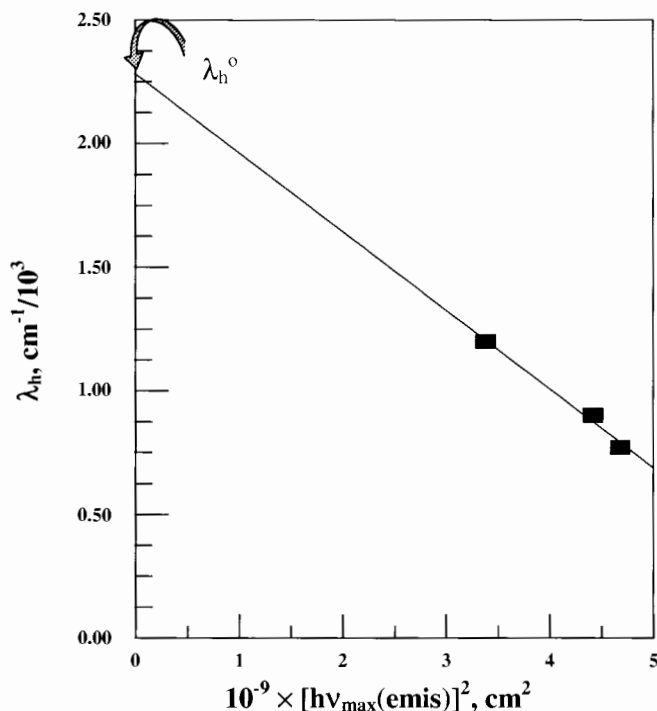


Figure 5. The attenuation of the molecular reorganizational energy contribution, λ_r , as a function of the delocalization of electronic charge. Based on the ratio of maximum intensities of the first and second resolved emission components: $\lambda_h = h\nu_h(I_{j=0}/I_{j=1}) = h\nu_h S_h$ [see equation (2)]. Assuming that $\lambda_h = \lambda_h^0(1 - 4\alpha_{LD}^2)$, and $\alpha_{LD} = H_{DL}/h\nu_{\max}(\text{emis.})$.

This is illustrated in Fig. 5 based on intensities determined at the emission maxima. Figure 5 implies that $\lambda_h^0 \cong (2280 \pm 150) \text{ cm}^{-1}$ and $H_{DL} \cong (6 \pm 1) \times 10^3 \text{ cm}^{-1}$. The inferred value of H_{DL} is in excellent agreement with that inferred for $\text{Ru}^{\text{II}}/\text{bpy}$ complexes based on other considerations [27]. The high frequency mode contributions to the reorganizational energy of these complexes is strongly attenuated with increasing delocalization of electron density.

EXCITED STATE LIFETIME BEHAVIOR

The connection between kinetic and spectroscopic parameters has been mentioned above and discussed extensively in the literature [4, 5, 7, 11, 12, 16, 19, 36, 59–62]. In principle, the MLCT excited state lifetimes can be correlated in terms of the reorganizational and E_{DA}^{00} parameters discussed above. In practice, the proposed relaxation mechanisms of the MLCT excited states of Ru-polypyridyls have usually involved the internal conversion between the MLCT and the metal-centered, dd excited states [63–66]. Most of the reported work has been in ambient aqueous solutions, much of it has been photochemical and few of the ammine complexes are

believed to luminesce. The lifetimes of the three complexes discussed here decrease roughly as the number of coordinated NH moieties increases. This suggests an important role of the NH vibrational modes in deactivating the MLCT excited states of these complexes. This issue is currently under investigation.

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