

Picosecond Raman Scattering Study of Electron Localization in the Charge-Transfer Excited State of Tris(bipyridine)ruthenium(II)

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Abstract: The picosecond time resolved resonance Raman spectra of the MLCT excited state have been observed in room temperature water, in isopropyl alcohol, in 4:1 ethanol/methanol above and below the glass transition temperature, and in anionic SDS micelles. In all cases the excited electron is localized on one bipyridine ligand. The vibrational relaxation-localization process appears to be complete within a few picoseconds. A broadening of MLCT Raman lines at high field intensities is attributed to nonlinear resonance scattering. Localization and subsequent electron hopping are discussed with use of the simple Franck-Condon electron transfer model for weakly coupled, mixed valence compounds.

Woodruff and co-workers^{1,2} as well as Forster and Hester³ established the remarkable fact that the lowest metal-to-ligand charge-transfer (hereafter MLCT) excited electronic state of tris(bipyridine)ruthenium(II), in aqueous solution at room temperature, can be characterized as $\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy})^-$. The excited electron is fully localized on one of three equivalent ligands, at least for a time long enough for this ligand and its neighboring solvent to adjust to the geometry of fully charged bpy^- . Localization was proven through analysis of the nanosecond MLCT excited state resonance Raman (hereafter RR) spectra. This result has been confirmed by subsequent optical experiments.⁴⁻⁶ This early experiment was a clear demonstration of the value of time resolved Raman spectroscopy in structural characterization of short-lived species.

In approximate terms, localization occurs if the vibrational and solvation energy released is significantly larger than the electron exchange energy between ligands. In this paper we investigate whether the vibrational relaxation-localization process can be time resolved on the ps scale and whether the solvation energy plays a significant role. The $\text{Ru}(\text{bpy})_3^{2+}$ MLCT dynamics in different local solvation environments have been intensively investigated in recent years (references 1-21 are a fraction of the recent literature). There are reports that localization does *not* occur in frozen, rigid environments,⁷⁻¹⁰ suggesting that localization requires

significant excited state solvation.

We carefully investigate the high resolution Stokes and anti-Stokes MLCT aqueous Raman scattering at room temperature in a search for possible disequilibrium with the solvent on the ≈ 10 ps time scale. In a search for solvation effects, we explore the ps (picosecond) Raman spectra in isopropyl alcohol, in SDS micellar solution, and above and below the glass temperature in 4:1 ethanol/methanol. We find that in all cases the MLCT state is localized. This result is discussed in terms of the simple Marcus model for localization previously developed for weakly coupled mixed-valence compounds.²²

Experimental Section

Our apparatus has been described recently.²³ The Nd:YAG mode locked laser system generates ≈ 25 ps pulses at a 10-Hz rate. In many experiments a single 355-nm pulse serves to both create the MLCT state and generate its Raman spectrum, as originally described on the nanosecond scale by Woodruff and co-workers.^{1,2} In some experiments a two-color, two-pulse pump and probe experiment is performed.

Extensive signal averaging is performed with a single stage 0.64 m spectrograph and a PAR 1420 intensified Reticon array detector. With a 3600 g/mm grating our instrumental resolution is 5 cm^{-1} (FWHM) near 355 nm. The Raman collection lens is in a near back scattering geometry with respect to the excitation beam. Room temperature aqueous experiments are performed on a vertically falling, 2-mm diameter solution stream in order to minimize scattered laser light. Low-temperature experiments are carried out in a Air Products Cryostat.

Results

A. Water and Isopropyl Alcohol at 293 K. The S_0 ground and MLCT excited state RR spectra at 355 nm have been analyzed in some detail.^{2,12,13,17} The neutral byp ligand and the anion bpy^- ligand both show significant resonance at 355 nm. The S_0 spectrum consists of byp lines. The MLCT spectrum consists of bpy^- lines and byp lines almost indistinguishable from S_0 lines.

A high fluence ≈ 10 -ns, 355-nm pulse almost quantitatively pumps the S_0 state to the long-lived (~ 600 ns) MLCT state and generates its Raman spectrum,^{1,2} as shown in Figure 1. We find that a 25-ps pulse of the same fluence yields almost the same spectrum, as shown in the figure.¹¹ There are no new lines, and the same sequence of conversion from S_0 to MLCT as a function of fluence is observed as in the nanosecond experiments.

It appears then that vibrational relaxation of the resonantly enhanced modes, and localization, are complete within the optical pulse width of 25 ps. Previous ps Raman experiments on excited states in liquids have also shown vibrational relaxation to be complete within a few picoseconds.^{24,25} Close inspection of the figure shows that the ps MLCT spectra are uniformly *broader*

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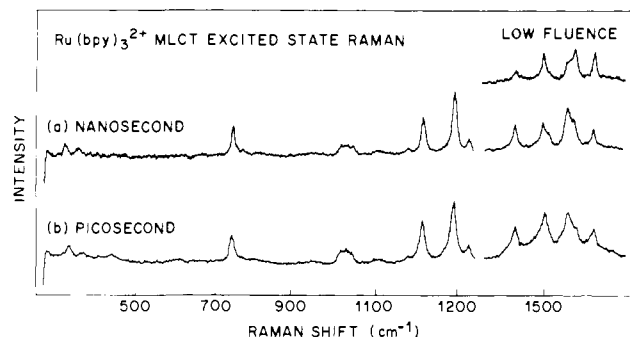


Figure 1. Nanosecond and picosecond resonance Raman spectra of the MLCT excited state in aqueous solution. The low fluence insert shows the ground-state spectrum (principally) in the high centimeter⁻¹ region.

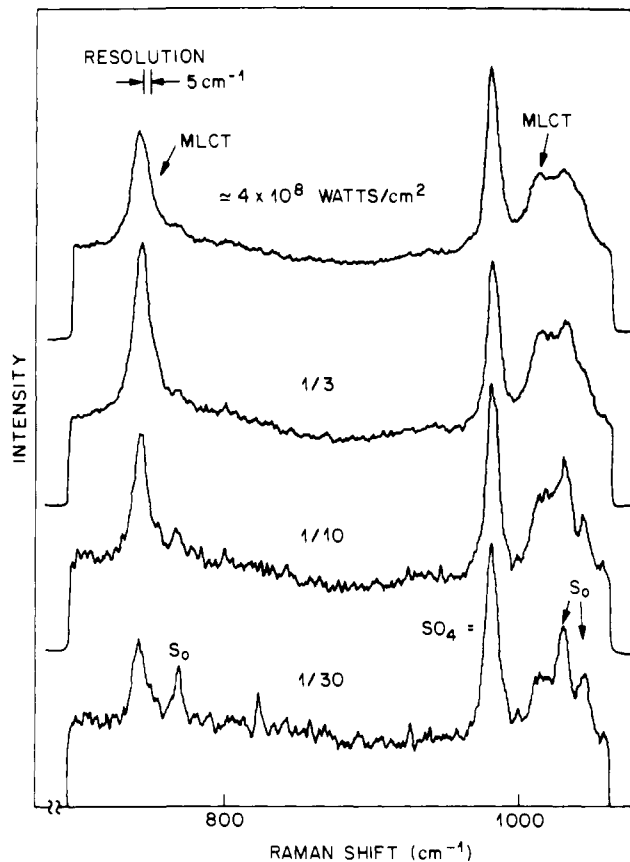


Figure 2. High resolution spectrum of the MLCT 744-cm⁻¹ transition in comparison with a SO₄²⁻ line (0.5 M), as a function of peak power. The lowest panel also shows several ground-state lines.

than the ns (nanosecond) spectra. This broadening of high frequency modes might reflect unrelaxed low-frequency motion in the molecule or the surrounding solvent. We therefore examined the low frequency Stokes and anti-Stokes Raman spectra for evidence of disequilibrium with the solvent. Unfortunately there are no low-frequency modes that show strong resonance at 355 nm, either in the ps or ns spectra. Careful examination of the anti-Stokes scattering in the 300-cm⁻¹ region shows no detectable transitions on top of the water continuum, in either the ps or ns spectra.

The growth and broadening of an MLCT line as a function of fluence is shown at high resolution in Figure 2. This figure shows the 744-cm⁻¹ transition in comparison with an internal standard SO₄²⁻ 984-cm⁻¹ line. Figure 3 is a log-log plot of intensity versus peak power, for both Raman lines. In the limit of a weak 355-nm beam (no saturation), the MLCT intensity should grow quadratically with fluence, while the SO₄²⁻ line should grow linearly. At very low flux, well below $\approx 10^8$ W/cm², this behavior is roughly observed. At high flux near 10^9 W/cm², the SO₄²⁻ line grows

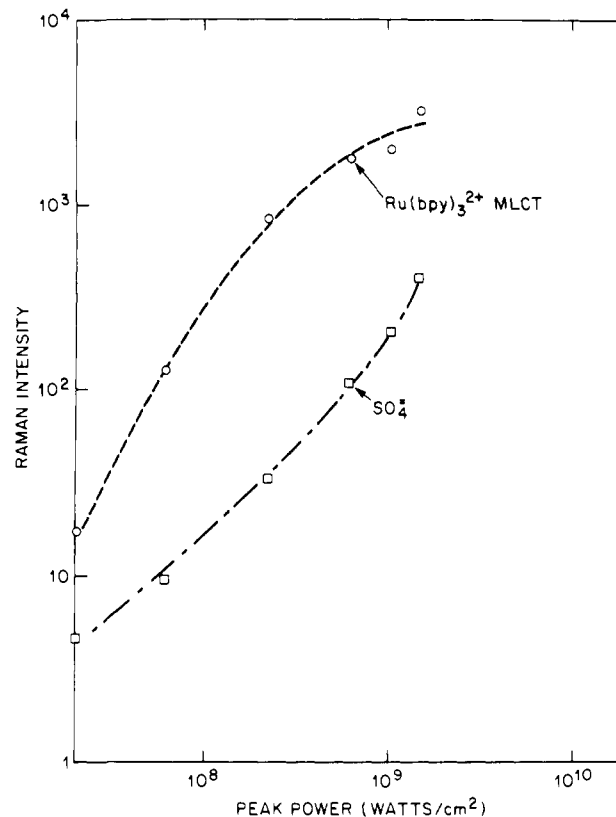


Figure 3. Log-log plot of the MLCT 744-cm⁻¹ transition integrated intensity, and the SO₄²⁻ integrated intensity, as a function of peak power. The two lines are drawn as guides for the eye.

supralinearly, and the MLCT line grows *sublinearly*. Over this same range the SO₄²⁻ line width does not change, while the instrumentally deconvoluted MLCT line width grows continuously from ≈ 5 cm⁻¹ at low flux to ≈ 14 cm⁻¹ at $\approx 1.5 \times 10^9$ W/cm².

The MLCT absorption cross section is fourfold higher than the S₀ cross section at 355 nm. If the pulse is intense enough to excite all S₀ to MLCT over a period 25 ps, then each MLCT state will itself absorb a second 355 photon ≈ 6 ps after its creation. If this doubly excited Ru(bpy)₃²⁺ molecule quickly relaxed back to MLCT and then absorbed a third photon from the same pulse, and so on, the SO₄²⁻ intensity would grow *sublinearly* with fluence, because MLCT attenuates the 355-nm beam more than S₀. This behavior is not observed. Supralinear SO₄²⁻ growth implies that population is lost from the MLCT state at high flux and also that the resonance Raman spectrum of MLCT is observed very roughly 6 ps after creation when the peak power is $\approx 10^9$ W/cm².

The MLCT systematic broadening at high flux is quite similar to broadening observed recently in the ground electronic state of β -carotene in isopentane.²⁶ In that case, a two-pulse, two-color Raman experiment proved that the broadening is due to high optical field and not to unrelaxed low frequency molecular or solvent motions. It is a manifestation of *nonlinear* resonant scattering²⁷ and is roughly analogous to power broadening. Simple calculations as previously outlined²⁶ show that broadening will occur in the MLCT RR spectra at $\sim 10^9$ W/cm², if the 355-nm beam is in resonance with a vibronic transition of oscillation strength ~ 0.1 . As the bpy⁻ π - π^* transition at 355 nm is strongly allowed ($\epsilon \approx 25000$ L/mol-cm), oscillator strengths of this magnitude are likely, and we tentatively assign the observed broadening in Ru(bpy)₃²⁺ to nonlinear resonant scattering.

The MLCT spectra thus appear to suggest that localization and relaxation are complete with ~ 6 ps. As alcohols have longer longitudinal relaxation times that have been implicated in some electrostatic solvation processes, we repeated these experiments

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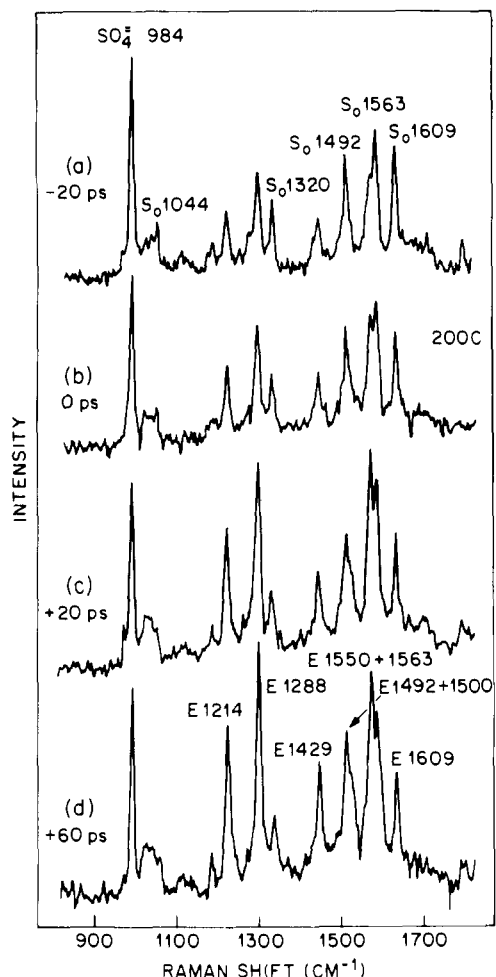


Figure 4. Time-resolved 355-nm Raman spectra as described in the text. The quoted time for each panel is the delay of the weak 355-nm pulse with respect to the intense 447-nm pulse. In panel (a), the 355-nm pulse precedes the 447-nm pulse, and the S_0 spectrum is seen. There is minor contribution of the MLCT to (a), caused by 355-nm excitation.

in isopropyl alcohol. Essentially the same MLCT RR line shapes and positions were observed. The ns spectra were the same as the high flux ps spectra (excluding nonlinear broadening).

Picosecond Raman scattering at low field can be observed by separating the excitation process from the scattering process in a two-color, two-pulse experiment. In Figure 4 a weak 355-nm pulse generates RR spectra following 447-nm excitation of the MLCT state. The MLCT state (labeled E here) appears roughly within the time convolution of the two ≈ 25 -ps laser pulses. The experimental resolution is ≈ 9 cm^{-1} FWHM, and no MLCT broadening is apparent. Because of the time convolution, the MLCT state is observed at a greater delay in these two pulse experiments than in the case of the ~ 6 ps delay for an intense 355 pulse.

B. 4:1 Ethanol/Methanol above and below the Glass Temperature. As mentioned in the introduction, some workers have inferred, from Raman and fluorescence data, that the MLCT state does not localize in rigid media. Krausz reported the characteristic localized RR spectrum to change into continuum scattering below the glass transition in 1:1 water/glycol, indicating no localization.⁷ Ferguson and Krausz argue from luminescence spectra that both solvent reorganization and localization stop (at different rates) below the glass temperature in 4:1 ethanol/methanol and in other glass formers.⁸⁻¹⁰ However, Kliger and co-workers argue from ns transient absorption spectra that the MLCT state is localized below the glass temperature in 4:1 ethanol/methanol.⁶ Photo-selection experiments also have been interpreted to indicate localization in frozen rigid environments.⁴

Figure 5 shows MLCT ps RR spectra at a resolution of 9 cm^{-1} in 4:1 ethanol/methanol. Parts of the spectra are absent due to

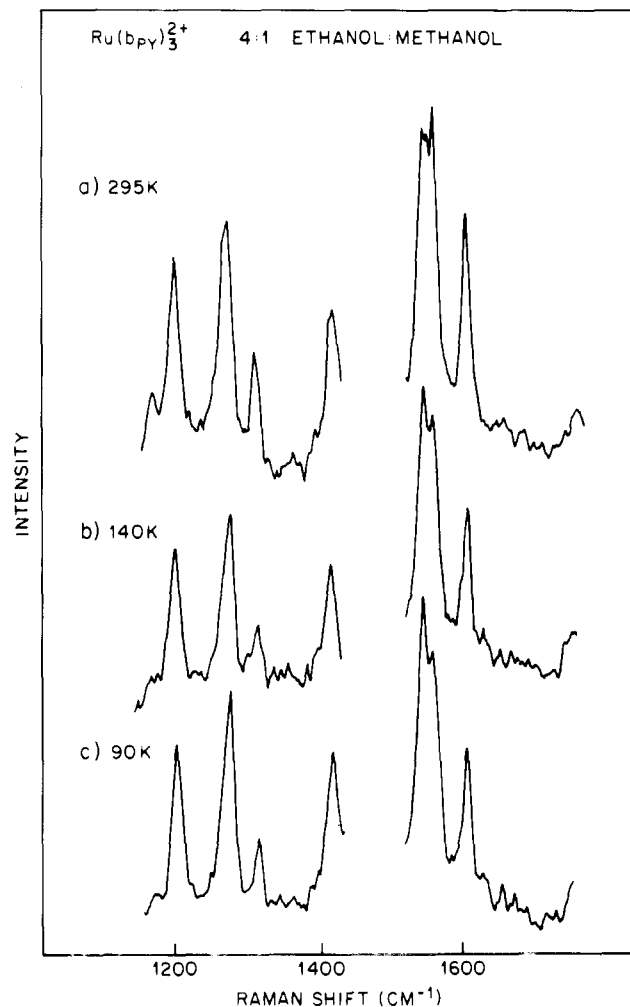


Figure 5. Picosecond MLCT RR spectra in 4:1 ethanol/methanol as a function of temperature. The solvent glass transition temperature is approximately 130 K.

intense alcohol lines at these positions. At our present sensitivity and resolution, we can detect no difference in the spectra, or the excited state yield at a given 355-nm flux, above and below the glass temperature. We conclude that the MLCT state is localized following 355-nm excitation at 90 K below the glass temperature. Higher resolution studies of the two MLCT lines at 1288 and 1214 cm^{-1} show no apparent line shape change below the glass temperature.

However, the MLCT luminescence spectra clearly show different vibronic line shapes and positions above and below the glass temperature.⁸⁻¹⁰ This result most reasonably implies, as previously concluded, that orientational resolution stops below the glass temperature. A marked change in emission spectra and lifetime are also reported for Ru(bpy)₃²⁺ adsorbed negatively charged SDS micellar surfaces,¹⁹⁻²¹ and we therefore decided to investigate this special solvation environment.

C. SDS Micelles. Ru(bpy)₃²⁺ strongly associates with the negatively charged surfaces of SDS (sodium dodecyl sulfate) aqueous micelles. Kinetic studies of MLCT luminescence in SDS micelles have correlated changes in the radiationless transition rates and luminescence spectra with solvation changes.¹⁹⁻²¹ In this regard, previous ns time resolved Raman experiments on tetrathiafulvalene and tetramethylbenzidine radicals in micelles have shown that local solvation effects sometimes produce small shifts in RR intensities and frequencies.^{28,29} Figure 6 shows the high flux ps 355 nm MLCT RR spectra in SDS micelles in

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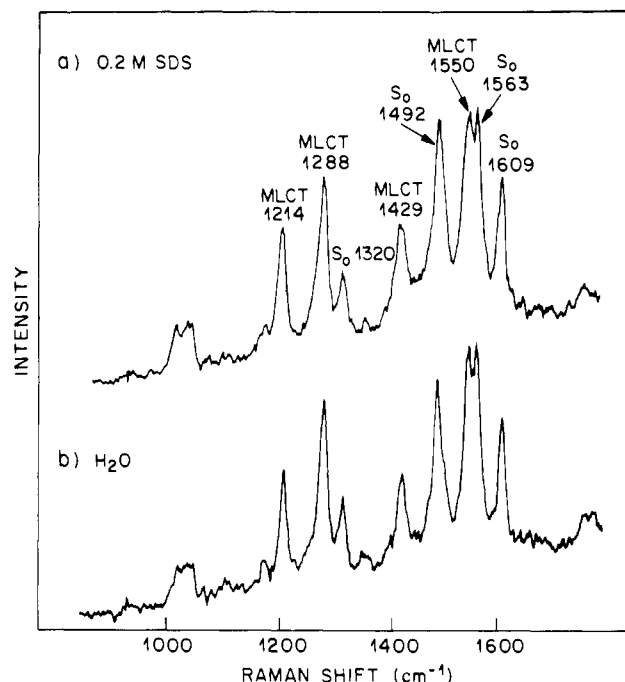


Figure 6. Picosecond MLCT RR spectra in 0.2 M SDS and in water.

comparison with aqueous spectra. At present resolution, there are no discernable relative intensity or bands shape changes. The MLCT state is localized on one ligand, as in the previous sections. We do observe that the MLCT intensity to be a factor of 4 weaker in the SDS micelle than in water, under conditions of the same flux and concentration. This result implies there is a higher loss yield for the MLCT state when it absorbs a 355-nm photon in the SDS micelle than in water. This observation may be related to the lowering of ionization potentials in SDS micelles.^{28,29}

Discussion

The organic glass and SDS micellar results demonstrate an interesting result; namely, that a combination of time resolved electronic and Raman experiments is more powerful than a simple sum of the individual results. The Raman experiments probe intramolecular vibrational structure and in this excited state $\text{Ru}(\text{bpy})_3^{2+}$ case unambiguously demonstrate localization on the photon scattering time scale $\sim 10^{-13}$ s. On the 10^{-11} s laser pulse width time scale, no precursors to the localized MLCT state have been observed, and vibrational relaxation of the resonantly enhanced modes appears to be complete. With this result, the previous luminescence vibronic line shape and decay measurements then indirectly reflect local solvation kinetics, confirming previous interpretations. The excited state electronic wave function is experimentally more sensitive to solvation than is the ground-state vibrational structure.

The reduced, ground-state species $\text{Ru}(\text{bpy})_3^+$ is also known to have a localized structure $\text{Ru}^{\text{II}}[\text{bpy}]_2[\text{bpy}]^-$,³⁰ and provides a structural model for the MLCT state. In $\text{Ru}(\text{bpy})_3^+$, ESR measurements show how the electron hops from ligand to ligand

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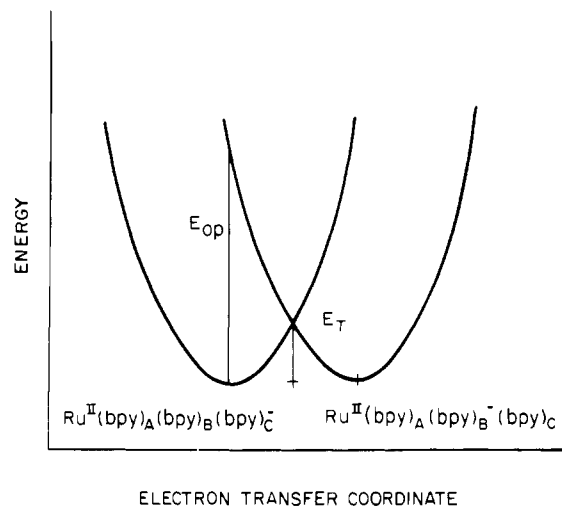


Figure 7. Schematic outline of Marcus electron transfer potential energy surfaces, after ref 22. E_T is the thermal barrier to electron transfer. E_{OP} is the most probable optical electron transfer energy.

on a 10^{-10} s time scale at room temperature, with an activation energy of ≈ 1000 cm^{-1} in CH_3CN .³¹ As diagrammatically shown in Figure 7 and reviewed in ref 22, there is a thermal barrier E_T to electron transfer originating in the vibrational Franck-Condon factors between initial and final states. This same compound shows a weak infrared charge-transfer transition³² at a fourfold higher energy ($E_{OP} \approx 4000$ cm^{-1}), in agreement with the simple Marcus electron transfer model for symmetrical, weakly coupled mixed-valence compounds.

In principal the vibrational trapping energy that localizes the e^- on one ligand has both intramolecular and solvation components. The frozen environment RR experiments imply that the intramolecular component is sufficient. In a mixed-valence compound of this sort, localization is a function of experimental time scale. Resonance Raman scattering measures the $\sim 10^{-13}$ s structure. Fluorescence polarization measures localization on the fluorescence lifetime, which is $\approx 10^{-6}$ s for the MLCT state. The photoselective experiments of Carlin and De Armond⁴ indicate that the hopping time may be longer than 10^{-6} s at liquid N_2 temperatures.

Recent detailed modeling of the radiationless decay and emission spectra of many metal polypyridine complexes have given estimates of the excited state vibrational and solvation reorganization energy following optical creation of the relaxed MLCT state.^{15,16} Within the confines of the simple Figure 7 Marcus theory, this reorganization energy is twice the thermal barrier to electron hopping in the MLCT state. The fitted reorganization energy is ≈ 3200 cm^{-1} in room temperature aqueous solution,^{15,16} suggesting a MLCT thermal barrier E_T somewhat larger than the 1000 cm^{-1} value in acetonitrile solutions of $\text{Ru}^{\text{II}}[\text{bpy}]_2[\text{bpy}]^-$.³¹

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