

Electron Transfer in Frozen Media

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Classical theories of electron transfer are modified to take into account the differences between electron transfer in a rigid medium and in a fluid. Intramolecular vibrations and part of the dielectric polarization are assumed to remain dynamic in rigid media while the remaining part of the polarization, arising from dipole reorientations, is frozen. In rigid media, electron transfer occurs with the solvent locked into the dipole orientations of the initial state. This causes an increase in the free energy change and a decrease in the solvent reorganizational energy. It also increases the activation free energy for electron transfer. For photoinduced electron transfer, the analysis is more complex because multiple states are involved. The activation free energy can either be greater or less than in a fluid depending on charge distributions before and after electron transfer. The same analysis can be applied to interconversion between excited states in rigid media.

Electron transfer reactions that are rapid in fluid solution often cease in a rigid medium—a glass, a plastic, or the solid state.^{1,2} One exception occurs in the reaction centers of photosynthetic bacteria where photoinduced electron transfer continues to occur even at 4 K.³ Another is in highly exergonic, bimolecular electron transfer reactions where the reactions are induced by photoexcitation or pulse radiolysis.⁴ In more recent studies, molecular assemblies have been designed which continue to undergo electron transfer in rigid media by increasing the driving force.^{5–7}

The rigid medium effect exists because large amplitude, orientational motions of the solvent dipoles are coupled to electron transfer and contribute to the reorganizational barrier.⁸ When these motions are frozen, their role changes and they

become part of the free energy change.^{5,6} The effect can be particularly large if the reactants and products differ significantly in their charge distributions.

If electron transfer in solution is sufficiently rapid, solvent dynamics can contribute to the rate, the slowest part being changes in dipole orientations.^{9,10} In some cases correlations have been found between rate constants or preexponential factors and solvent relaxation times.¹⁰ In rigid media the orientational motions are frozen and do not contribute to the dynamics. The energetics change because electron transfer occurs with solvent dipoles in the orientations of the initial state. The products formed in these orientations are at high energy compared to solution. Part of the solvent reorganizational energy is added to the free energy change decreasing the solvent reorganizational energy.

Theories of electron transfer in fluid solution must be modified to take into account these effects. In earlier papers we described the rigid medium effect and presented experimental evidence for the importance of the driving force.⁵ The change from reorganizational energy to energy gap was recognized and the existence of a rigid medium “inverted effect” identified. Wasilewski et al. presented an extensive set of data demonstrating the rigid medium effect and quantifying the role of driving force.⁶

In our original analysis, the effect of intramolecular vibrations and the dynamical part of the solvent polarization in rigid media were neglected.^{5a} Here, we return to this problem, applying results obtained in a paper by Marcus^{11a} and elaborate in further detail on the effects of rigid media on electron transfer.

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Analysis

Excited State Energetics in Rigid Media. Marcus has used dielectric continuum theory to analyze the effect of rigid media on charge transfer absorption and emission.¹¹ From his analysis, the emission energy in a frozen medium, $E_{\text{em,fr}}$, is given in the classical limit by

$$E_{\text{em,fr}} = E_{\text{fl}}(0-0) + \lambda_{\text{oo}} - \lambda_i - \lambda_{\text{oi}} \quad (1)$$

$E_{\text{fl}}(0-0)$ is the 0-0 energy difference (or free energy difference, ΔG° , in certain limits)¹² between the ground and excited states in the fluid and λ_i is the intramolecular reorganizational energy. The solvent reorganizational energy (λ_o) is partitioned into λ_{oi} and λ_{oo} . λ_{oi} arises from translational, phonon-like lattice modes which manifest themselves as density fluctuations and remain dynamical in rigid media.^{11b} The intramolecular vibrations remain dynamical as well. λ_{oo} arises from collective dipole rotations or reorientations which are frozen in rigid media. Following optical excitation, excited states are formed surrounded by dipole orientations characteristic of the ground state but at equilibrium in the intramolecular and translational modes. This increases $E(0-0)$ in rigid media by λ_{oo} and E_{em} by $2\lambda_{\text{oo}}$ compared to the fluid, eqs 2 and 3. The latter effect has been observed experimentally.¹³⁻¹⁶

$$E_{\text{fr}}(0-0) = E_{\text{fl}}(0-0) + \lambda_{\text{oo}} \quad (2)$$

$$E_{\text{em,fr}} = E_{\text{em,fl}} + 2\lambda_{\text{oo}} \quad (3)$$

If the solvent is treated as a dielectric continuum and the solute as a hard, spherical cavity of radius a , λ_{oo} and λ_{oi} are given by

$$\lambda_{\text{oo}} = \frac{(\bar{\mu}_f - \bar{\mu}_i)^2}{a^3} \left[\frac{1 - D_{\text{s,fr}}}{2D_{\text{s,fr}} + 1} - \frac{1 - D_{\text{s,fl}}}{2D_{\text{s,fl}} + 1} \right] \quad (4a)$$

$$\lambda_{\text{oi}} = \frac{(\bar{\mu}_f - \bar{\mu}_i)^2}{a^3} \left[\frac{1 - D_{\text{op}}}{2D_{\text{op}} + 1} - \frac{1 - D_{\text{s,fr}}}{2D_{\text{s,fr}} + 1} \right] \quad (4b)$$

In these equations, $\bar{\mu}_i$ and $\bar{\mu}_f$ are the dipole moments of the initial and final states, D_{op} is the optical dielectric constant, and $D_{\text{s,fr}}$ and $D_{\text{s,fl}}$ are the static dielectric constants of the frozen and fluid solutions, respectively. The internal dielectric constant of the solute is taken to be one. An equivalent set of equations can be written for a single electron transfer between spheres of radii a_1 and a_2 separated by a distance d

$$\lambda_{\text{oo}} = e^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \left(\frac{1}{D_{\text{s,fr}}} - \frac{1}{D_{\text{s,fl}}} \right) \quad (5a)$$

$$\lambda_{\text{oi}} = e^2 \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d} \right) \left(\frac{1}{D_{\text{op}}} - \frac{1}{D_{\text{s,fr}}} \right) \quad (5b)$$

In these models the magnitudes of the energy shifts between the glass and fluid states in eq 4 depend on the change in dipole moment between initial and final states or the distance of

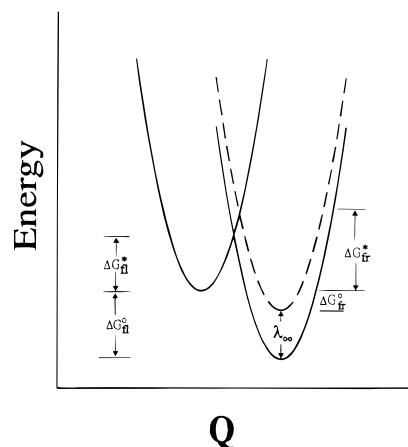


Figure 1. Energy-coordinate diagram assuming the harmonic oscillator approximation for a vibration or solvent mode coupled to electron transfer in fluid (solid line) or rigid (dashed line) media.

electron transfer, eq 5. Their magnitudes can be large for charge transfer transitions or for back-electron-transfer within molecular assemblies.^{5-7,13-15} On the other hand, the change in dipole moment for $\pi-\pi^*$ excited states, for example, is typically small and the difference in E_{em} between rigid and fluid media can be negligible. Energy shifts also depend on the difference between $D_{\text{s,fr}}$ and $D_{\text{s,fl}}$. For polar solvents, $D_{\text{s,fl}} \gg D_{\text{s,fr}}$ because dipoles are frozen and shifts in E_{em} are large. For nonpolar solvents, $D_{\text{s,fl}} \sim D_{\text{s,fr}}$ and shifts are small. All of these conclusions have been demonstrated experimentally.¹³⁻¹⁶

Electron Transfer in Rigid Media. According to the classical theories of Marcus, Hush, and Sutin, the electron transfer rate constant in *fluid* solution is given by^{8,17,18}

$$k_{\text{ET}} = \nu_{\text{ET}} \exp(-\Delta G^*/RT) \quad (6)$$

ν_{ET} is the product of κ , the transmission coefficient, and ν_n , the effective nuclear frequency. ΔG^* is the activation free energy, R the gas constant, and T the absolute temperature. The activation free energy is given by

$$\Delta G^* = (\lambda + \Delta G_o)^2/4\lambda \quad (7)$$

ΔG_o is the free energy change and λ the total reorganizational energy, $\lambda_i + \lambda_o$.

In the classical theories, electron transfer requires reorganization along certain vibrational and solvent coordinates in order to reach the intersection between energy surfaces. This is illustrated in Figure 1. At the intersection, the energies of the reactants and products are equal and electron transfer can occur with energy conservation. If nuclear coordinates remain in equilibrium at the intersection, electron transfer is nonadiabatic, and $\kappa < 1$. The dynamics of electron transfer depend on the extent of electronic coupling, and the preexponential factor in eq 6. The latter depends on the square of the electron transfer matrix element (H_{DA}).

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$$\nu_{\text{ET}} = \kappa \nu_n = \frac{2\pi H_{\text{DA}}^2}{\hbar} \left(\frac{1}{4\pi\lambda RT} \right)^{1/2} \quad (8)$$

When electron transfer at the intersection is rapid compared to the nuclear dynamics, equilibrium can not be maintained and electron transfer is coupled with, or even controlled, by nuclear dynamics. When this occurs, $\kappa = 1$, electron transfer is adiabatic, and the preexponential term becomes ν_n . ν_n is given by a weighted average of nuclear frequencies for all the normal modes that contribute to λ .^{17,18} The solvent reorientational modes are relatively slow. When they dominate, correlations exist between ν_n or k_{ET} and the longitudinal relaxation time in fluid solution.^{9,10}

In a frozen medium, the reorientational modes no longer play a dynamical role and ν_n increases from the $\sim 10^{12} \text{ s}^{-1}$ relaxation time for a typical polar organic solvent, to $\sim 10^{13} \text{ s}^{-1}$, the weighted average of solvent translational modes and intramolecular vibrations. This means that the magnitude of H_{DA} required to reach the onset of adiabatic electron transfer is increased by ~ 3 .

In a frozen medium, electron transfer occurs at fixed solvent orientations and the products are formed at a higher energy than in the fluid. This is shown in Figure 1 by the decrease in driving force ($-\Delta G^\circ$). The part of the solvent reorganizational energy that is frozen, λ_{oo} , is added to the free energy change

$$\Delta G_{\text{fr}}^\circ = \lambda_{\text{oo}} + \Delta G_{\text{fl}}^\circ \quad (9)$$

The classical barrier to electron transfer in fluid solution, ΔG_{fl}^* , is given by

$$\Delta G_{\text{fl}}^* = \frac{(\lambda_i + \lambda_{\text{oi}} + \lambda_{\text{oo}} + \Delta G_{\text{fl}}^\circ)^2}{4(\lambda_i + \lambda_{\text{oi}} + \lambda_{\text{oo}})} = \frac{(\lambda + \Delta G_{\text{fl}}^\circ)^2}{4\lambda} \quad (10)$$

with $\lambda = \lambda_i + \lambda_{\text{oi}} + \lambda_{\text{oo}}$. ΔG^* is increased in a frozen medium $\lambda = \lambda_i + \lambda_{\text{oi}}$

$$\Delta G_{\text{fr}}^* = \frac{(\lambda_i + \lambda_{\text{oi}} + (\Delta G_{\text{fl}}^\circ + \lambda_{\text{oo}}))^2}{4(\lambda_i + \lambda_{\text{oi}})} = \frac{(\lambda + \Delta G^\circ)^2}{4(\lambda_i + \lambda_{\text{oi}})} \quad (11)$$

The two are related by

$$\Delta G_{\text{fr}}^* = \left(\frac{\lambda_i + \lambda_{\text{oi}} + \lambda_{\text{oo}}}{\lambda_i + \lambda_{\text{oi}}} \right) \Delta G_{\text{fl}}^* = \left(1 + \frac{\lambda_{\text{oo}}}{\lambda_i + \lambda_{\text{oi}}} \right) \Delta G_{\text{fl}}^* \quad (12)$$

The difference between them increases with λ_{oo} .

If ion-pairing is important and ion motions frozen, there is an additional contribution to the free energy change, λ_{IP} .^{19ab} The magnitude of λ_{IP} depends on the change in electrostatic interactions between ions in the initial and final states. In this case ΔG_{fr}^* is given by^{19c}

$$\Delta G_{\text{fr}}^* = \frac{(\lambda_i + \lambda_{\text{oi}} + (\Delta G_{\text{fl}}^\circ + \lambda_{\text{oo}} + \lambda_{\text{IP}}))^2}{4(\lambda_i + \lambda_{\text{oi}})} \quad (13)$$

Photoinduced Electron Transfer in Rigid Media. Photoinduced electron-transfer is more complicated because multiple

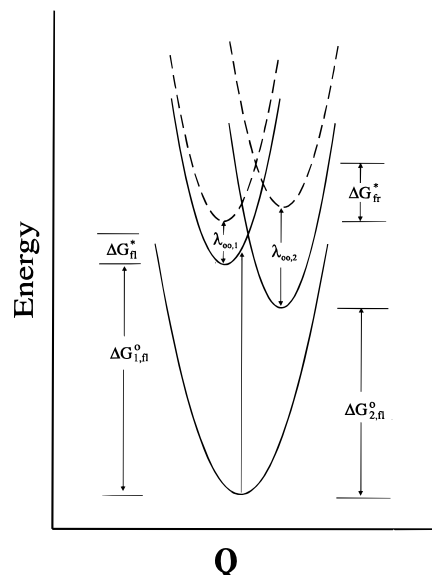
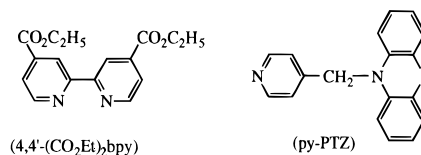
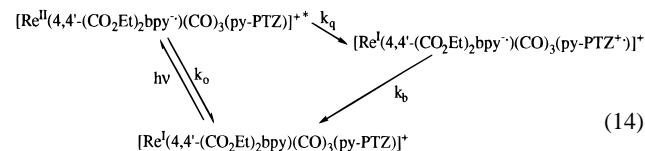


Figure 2. Energy-coordinate diagram for photoinduced electron transfer in a three-state system in fluid (solid lines) and rigid (dashed line) media.

states are involved, the ground state and the states undergoing electron transfer. An example of a three-state system is illustrated in the energy diagram in Figure 2. This would be the case for back electron-transfer in a chromophore-quencher complex such as $[\text{Re}^{\text{II}}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^-)(\text{CO})_3(\text{py-PTZ}^+)]^+$ in a 4:1 EtOH/MeOH glass at 77 K, or in a rigid plastic at room temperature, eq 14.^{5b} There are two sets of energy-coordinate



curves in Figure 2. They describe a classical intramolecular vibration or coupled solvent mode treated as an harmonic oscillator in a fluid (solid line) or frozen (dashed line) medium.

Initial excitation gives the metal-to-ligand charge transfer (MLCT) excited state, $\text{Re}^{\text{II}}(4,4'-(\text{CCO}_2\text{Et})_2\text{bpy}^-)$, frozen in the nuclear coordinates of the ground state. Subsequent relaxation occurs in the intramolecular vibrations and solvent translational modes to give a state of energy $\Delta G_{\text{fl}}^* = \Delta G_{\text{fl}}^\circ + \lambda_{\text{oo},1}$. ΔG_{fl}^* is the free energy of the thermally equilibrated excited state above the ground state in the fluid. $\lambda_{\text{oo},1}$ is the frozen part of the solvent reorganizational energy between $\text{Re}^{\text{II}}(\text{bpy}^-)$ and the ground state. Similarly, the energy of the second state is $\Delta G_{\text{fr}}^* = \Delta G_{\text{fl}}^* + \lambda_{\text{oo},2}$. $\Delta G_{\text{fl}}^\circ$ and $\lambda_{\text{oo},2}$ are the same quantities for the second state. The driving force for electron transfer from $-\text{PTZ}$ to Re^{II} , $\Delta G_{\text{fr}}^\circ$, which interconverts the two upper states, is given by,

$$\Delta G_{\text{fr}}^\circ = (\Delta G_{\text{2,fl}}^\circ - \Delta G_{\text{1,fl}}^\circ) + (\lambda_{\text{oo},2} - \lambda_{\text{oo},1}) = \Delta(\delta G_{\text{ES,fl}}^\circ) + \Delta\lambda_{\text{oo}} \quad (15)$$

The free energy of activation in the classical limit is given by

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$$\Delta G_{\text{fr}}^{\ddagger} = \frac{(\lambda_i + \lambda_{oi} + \Delta G_{\text{fr}}^{\circ})^2}{4(\lambda_i + \lambda_{oi})} = \frac{(\lambda_i + \lambda_{oi} + \Delta(\Delta G_{\text{ES,fl}}^{\circ}) + \Delta\lambda_{oo})^2}{4(\lambda_i + \lambda_{oi})} \quad (16)$$

λ_i and λ_{oi} are the reorganizational energies for electron transfer between the upper states. If one assumes harmonic oscillators and equal force constants, $\Delta\lambda_{oo}$ is related to $\lambda_{oo,1}$ and $\lambda_{oo,2}$ by

$$\Delta\lambda_{oo} = \lambda_{oo,1} + \lambda_{oo,2} \pm 2(\lambda_{oo,1}\lambda_{oo,2})^{1/2} \quad (17)$$

According to eq 15 and 17, the driving force for photoinduced electron transfer in a frozen medium can be greater or less than in fluid solution depending on the sign of $\Delta\lambda_{oo}$.

The effect of $\Delta\lambda_{oo}$ on driving force has been demonstrated by Wasilewski et al. in 2-methyltetrahydrofuran at 77 K.⁶ They studied photochemical electron transfer in porphyrin–quinone, porphyrin–tetracyanoquinodimethane, and chromophore–quencher assemblies by laser flash photolysis. Following excitation of the porphyrin, intramolecular electron transfer occurred, and from the variation in k_{ET} with driving force, it was estimated that $\Delta\lambda_{oo} \sim 0.80 \pm 0.05$ eV.

The sign of $\Delta\lambda_{oo}$ depends on the solvent polarization in states 1 and 2 relative to the ground state. For the spherical cavity result in eq 4 with the ground state dipole moment 0 or negligible, $\Delta\lambda_{oo}$ is given by

$$\Delta\lambda_{oo} = \frac{(\bar{\mu}_2)^2 - (\bar{\mu}_1)^2}{a^3} \left[\frac{1 - D_{s,\text{fr}}}{2D_{s,\text{fr}} + 1} - \frac{1 - D_{s,\text{fl}}}{2D_{s,\text{fl}} + 1} \right] \quad (18)$$

If there is an increase in dipole moment in the second state, $|\bar{\mu}_2| > |\bar{\mu}_1|$, and $\Delta\lambda_{oo}$ is positive. In this case, the driving force is decreased in a frozen medium, $\Delta G_{\text{fr}}^{\circ} > \Delta G_{\text{fl}}^{\circ}$ and $\Delta G_{\text{fr}}^{\ddagger} > \Delta G_{\text{fl}}^{\ddagger}$. This would be the case for a $\pi\pi^* \rightarrow$ MLCT transition, for quenching of the porphyrin excited state in a porphyrin–quinone assembly, or for the –PTZ to Re^{II} intramolecular electron transfer in eq 14. If $|\bar{\mu}_2| < |\bar{\mu}_1|$, $\Delta G_{\text{fr}}^{\circ} < \Delta G_{\text{fl}}^{\circ}$ and the relative magnitudes of $\Delta G_{\text{fr}}^{\ddagger}$ and $\Delta G_{\text{fl}}^{\ddagger}$ depend upon $\Delta\lambda_{oo}$ in a complex way, eq 16.

Electron transfer is spontaneous, $\Delta G_{\text{fr}}^{\circ} < 0$, when

$$(\Delta G_{2,\text{fl}}^{\circ} + \lambda_{oo,2}) < (\Delta G_{1,\text{fl}}^{\circ} + \lambda_{oo,1}) \quad (19)$$

The inverted region occurs when

$$-[\Delta(\Delta G_{\text{ES,fl}}^{\circ}) + \Delta\lambda_{oo}] > (\lambda_i + \lambda_{oi}) \quad (20)$$

Further increases in driving force cause $\Delta G_{\text{fr}}^{\ddagger}$ to increase (and $\ln k_{\text{ET}}$ to decrease), quadratically with $\Delta G_{\text{fr}}^{\circ}$ in the classical limit, eq 6.

The dependence on $\Delta G_{\text{fr}}^{\circ}$ is different if medium or high frequency vibrations are coupled to electron transfer. In the single mode approximation with $\Delta G_{\text{fr}}^{\circ} \gg \lambda$ and $\hbar\omega \gg k_{\text{B}}T$ for the acceptor vibration, $\ln k_{\text{ET}}$ varies with $\Delta G_{\text{fr}}^{\circ}$ as^{20–22}

$$\ln k_{\text{ET}} \propto -\frac{\gamma}{\hbar\omega} |\Delta G_{\text{fr}}^{\circ}| \quad (21)$$

$$\gamma = \ln \frac{|\Delta G_{\text{fr}}^{\circ}|}{S\hbar\omega} - 1 \quad (22)$$

This is a form of the energy gap law. In eqs 21 and 22, $\hbar\omega$ is the quantum spacing and S the electron–vibrational coupling constant for the acceptor mode.

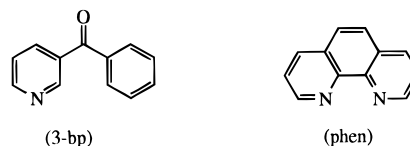
For $[\text{Re}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})(\text{CO})_3(\text{py-PTZ})]^+$ in a rigid poly-(methylmethacrylate) (PMMA) matrix at room temperature, $\text{Re}^{\text{I}} \rightarrow \text{bpy}$ excitation and intramolecular electron transfer are followed by back-electron-transfer, eq 14.^{5b} This reaction occurs in the inverted region, $\Delta G_{\text{fr},2}^{\circ} > (\lambda_{i,2} + \lambda_{oi,2})$, and gives the ground state. The rate constant for back-electron-transfer in PMMA (k_{ET} in eq 14) is decreased by ~ 42 compared to CH_3CN at room temperature. This is an energy gap effect and is predicted qualitatively by eq 21. The energy gap in PMMA compared to solution is increased by $\lambda_{oo,2}$

$$\Delta G_{\text{fr},2}^{\circ} = \Delta G_{2,\text{fl}}^{\circ} + \lambda_{oo,2} \quad (23)$$

which decreases $\ln k_{\text{ET}}$. The same effect exists for nonradiative decay and has been documented many times for MLCT excited states.^{14–16}

Interconversion between Excited States. The analysis applied to electron transfer also applies to interconversion between excited states of different orbital origins. In this case, the matrix element coupling the states originates in a vibration or vibrations of appropriate symmetry to mix the states—the promoting modes.²¹ The solvent influences the rate of interconversion between states if there are differences in charge distribution and equilibrium solvent polarizations.

In $[\text{Re}(3\text{-bp})_2(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{phen})(\text{CO})_3(\text{CH}_3\text{CN})]^+$, ligand-localized ($\pi\pi^*$ or $n\pi^*$) states exist which are slightly higher than the lowest MLCT states.^{23–25} In the interconversion



between states, e.g., $\pi\pi^*(\pi^1 d\pi^6 \pi^{*1}) \rightarrow \text{MLCT}(\pi^2 d\pi^5 \pi^{*1})$, there is a redistribution of electron density between $d\pi$ and π^* . In fluids, these interconversion are rapid. In frozen solutions, unperturbed emissions are frequently observed from both states, suggesting that ligand-localized \rightarrow MLCT interconversion occurs slowly, if at all. Similar observation have been made for other emitters where there are closely lying states.^{26–28}

Slow interconversion is a consequence of the increased activation barrier in the glass, eq 16. For these ligand-localized \rightarrow MLCT transitions, in eq 18, $|\bar{\mu}_2| > |\bar{\mu}_1|$ and $\Delta\lambda_{oo}$ is positive. This increases ΔG° , $\Delta G_{\text{fr}}^{\circ} > \Delta G_{\text{fl}}^{\circ}$ and increases ΔG^{\ddagger} , $\Delta G_{\text{fr}}^{\ddagger} > \Delta G_{\text{fl}}^{\ddagger}$.

By contrast only $\pi\pi^*$ emission is observed for *fac*- $[\text{Re}(4\text{-phenylpyridine})_2(\text{CO})_3\text{Cl}]$ in 2-propanol or EPA at 77 K, even though there is a closely lying MLCT state. This state dominates emission and excited state decay in fluid solution. A viable explanation for the change in behavior for this case is that the energy ordering is $\text{MLCT} > \pi\pi^*$ with rapid $\text{MLCT} \rightarrow$

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$\pi\pi^*$ interconversion occurring in the glasses. This is also consistent with eq 18 since in this case $|\bar{\mu}_2| < |\bar{\mu}_1|$ and the barrier to $\text{MLCT} \rightarrow \pi\pi^*$ interconversion is *less* in the rigid media.

The apparent inversion in excited state ordering between glass and fluid in the latter case may also be a rigid medium effect. It follows from eq 9 that the stabilization from glass to fluid is given by $\Delta G_{\text{fr}}^{\circ} - \Delta G_{\text{fl}}^{\circ} = \lambda_{\text{oo}}$. This favors the MLCT state in

the fluid because λ_{oo} varies with $(\Delta\bar{\mu})^2$, eq 4a, and $\Delta\bar{\mu}(\text{MLCT}) > \Delta\bar{\mu}(\pi\pi^*)$.

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