case, then these two forms of the trimer could be nearly isoenergetic. Calculations are under way to examine this possibility.

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Hole-Burning Spectroscopy of Polar Molecules in Polar Solvents: Solvation Dynamics and Vibrational Relaxation

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The time- and frequency-resolved hole-burning line shape of polar molecules in a polar solvent is expressed in terms of gas-phase spectroscopic parameters of the solute, vibrational relaxation rates, dielectric properties of the solvent, and the temporal profile of the pump pulse. At short times, a progression of narrow vibronic holes is predicted. As a consequence of solvent relaxation, these holes broaden and undergo a red shift. This behavior has been observed in the measurements of Shank et al. on cresyl violet in ethylene glycol. We propose hole burning as an alternative to fluorescence measurements in probing solvation dynamics.

Hole-burning (saturation spectroscopy) measurements with femtosecond time resolution of cresyl violet in ethylene glycol have recently been reported by Shank and co-workers.[1] In these experiments, the sample is excited with a 60 femtosecond pump pulse, and the absorption spectrum is measured with a 10 fs probe pulse. If the delay time between pump and probe is short, the absorption spectrum shows a decrease in absorption (hole) at the pump frequency, as is expected for a system with an inhomogeneously broadened absorption spectrum. In addition, two holes of smaller intensity occur 600 cm^{-1} to the red and to the blue of the central hole. Stimulated Raman measurements have shown that the dominant Raman-active vibration in cresyl violet has a frequency of 590 cm^{-1}.[2] As the delay between pump and probe is increased, the holes undergo substantial broadening and a red shift, and at a delay of 150 fs, the vibronic structure is lost and the hole width is comparable to the width of the entire absorption spectrum. The temporal evolution of the absorption spectrum is ascribed by Shank et al. to vibrational relaxation in cresyl violet. We have developed a theory of the hole-burning spectroscopy of a polar molecule in a polar solvent that includes both vibrational relaxation of the solute and the reorganization of the solvent about the electronically excited solute. We propose that the broadening and red shift of the vibronic holes in the cresyl violet spectrum may arise from the relaxation of solvent dipoles around the electronically excited dye molecule.

We consider a solution composed of solute and solvent molecules. The solute molecules are present in sufficiently low concentration that interactions among them are negligible, and we may treat a single solute in its solvent environment. The differential absorption spectrum, $\Delta\alpha(\omega_2)$, is defined to be the difference between the absorption coefficient at ω_2 in the absence of a pump pulse and the absorption coefficient at ω_2 measured with a probe pulse that follows a pump pulse. The differential absorption at ω_2 is related to $E_2(\omega_2)$, the amplitude of the probe field, and $\tilde{P}^{\mathrm{NL}}(\omega_2)$, the nonlinear polarization of the medium[3] by

$$\Delta\alpha(\omega_2) = -(4\pi\omega_2/c)\ \mathrm{Im}\ [\tilde{P}^{\mathrm{NL}}(\omega_2)/E_2(\omega_2)] \qquad (1)$$

$\tilde{P}^{\mathrm{NL}}(\omega_2)$ is the Fourier transform of $P^{\mathrm{NL}}(\tau)$, the nonlinear polarization of the medium at time τ.

$$\tilde{P}^{\mathrm{NL}}(\omega_2) = \int_{-\infty}^{\infty} \mathrm{d}\tau\ \exp(i\omega_2\tau) P^{\mathrm{NL}}(\tau) \qquad (2a)$$

$$P^{\mathrm{NL}}(\tau) = n\ \mathrm{Tr}\ \{\mu\rho^{\mathrm{NL}}(\tau)\} \qquad (2b)$$

ρ^{NL}, the nonlinear contribution to the density matrix, is the difference between the full density matrix and that part of the density matrix that is linear in the radiation–matter interaction. In eq 2b, μ is the transition dipole operator, n is the number density of solute molecules, and Tr denotes the trace. Substitution of the linear part of the density matrix into the right side of eq 2b yields the linear polarization, which, when inserted into the right side of eq 1, yields the absorption spectrum in the absence of a pump pulse. We shall evaluate ρ^{NL} to third order in the radiation–matter interaction[4,5] for the following model. The solute is taken to be a polyatomic molecule with two electronic states. The molecular energy levels are shown in Figure 1. The labels a and c denote vibronic states in the manifold of the ground electronic state of the solute, while b and d refer to vibronic states in the excited-state manifold. The influence of the solvent on $\Delta\alpha$ is expressed by the solvation coordinate $\hat{U}(t)$, an operator that represents the difference between the interactions of the solvent with the excited-state solute and with the ground-state solute

$$\hbar\ \hat{U}(t) = \exp(ih_e t/\hbar)\sum_m (V_m^{\mathrm{e}} - V_m^{\mathrm{g}})\ \exp(-ih_e t/\hbar) \qquad (3)$$

In eq 3, h_e is the Hamiltonian of the solvent in the presence of the electronically excited solute and V_m^{e} (V_m^{g}) is the interaction between the solvent molecule labelled m and the excited-state (ground-state) solute. We adopt a semiclassical approach in which the solute is treated quantum mechanically but the solvent is treated classically. We replace the operator $\hat{U}(t)$ by a stochastic variable $U(t)$, with mean $\langle U(t)\rangle$. Prior to the excitation of the

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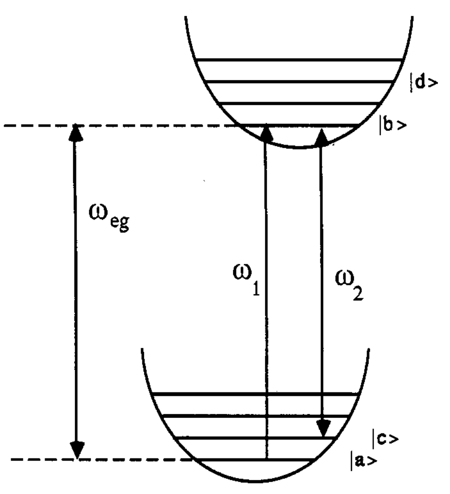

Figure 1. Molecular energy levels involved in hole burning. $|a\rangle$ and $|c\rangle$ denote vibronic states of the ground-state manifold, and $|b\rangle$ and $|d\rangle$ denote vibronic states of the excited-state manifold. ω_1 and ω_2 are the pump and probe frequencies, respectively. ω_{eg} is the frequency of the 0–0 absorption transition in the solvated molecule.

solute, the mean solvation coordinate is $\langle U(0)\rangle$. The solute is excited by the pump pulse at $t = 0$, and $\langle U(t)\rangle$ describes the relaxation of the mean solvation coordinate to its new value. Since $U(t)$ is composed of contributions from each of the solvent molecules, we invoke the central limit theorem and assume that $U(t)$ obeys Gaussian statistics. The correlation function of the fluctuations of U is given by

$$\langle \delta U(t + \tau)\delta U(\tau)\rangle \equiv \Delta^2 K(t); \quad K(0) = 1 \tag{4}$$

$$\delta U(t) \equiv U(t) - \langle U(t)\rangle \tag{5}$$

In the following derivation, we shall assume that the equilibrium configuration of the solvent depends on the electronic state of the solute but that the magnitude and time scale of the fluctuations about this equilibrium configuration are independent of the state of the solute. We assume that the fluctuations in the solvent environment of a solute are described by eq 4, whether the solute is in the ground or excited electronic states.

The experiment begins with the application of a pump pulse whose electric field, $E_1(t)$, is taken to have the Gaussian form

$$E_1(t) = 2\vartheta_1 \cos(\omega_1 t)(W/\pi^{1/2}) \exp(-W^2t^2) \tag{6}$$

After a delay time t_0, the absorption spectrum is measured with the probe pulse. We assume that the duration of the probe is sufficiently short that the nuclear degrees of freedom in the system do not undergo significant time evolution during the pulse. In this limit, the temporal profile of the probe pulse does not enter into $\Delta\alpha$. $\Delta\alpha$ can now be calculated according to the procedure that was recently developed[4] for the determination of the time- and frequency-resolved fluorescence spectrum of a polar, polyatomic molecule in a polar solvent. The result is

$$\begin{aligned}\Delta\alpha(\omega_2) = {} & (2\pi)^{3/2}(\omega_2/c)(\vartheta_1{}^2 n/\hbar^3\Delta)\frac{W}{[W^2 + \Delta^2(1 - K^2(t_0))]^{1/2}} \times \\ & \sum_{a,b,c,d} |\mu_{ab}|^2|\mu_{cd}|^2 P(a) \exp\left\{\frac{-(\omega_1 - \omega_{eg} - \omega_{ba})^2}{2(\Delta^2 + W^2)}\right\}\{G_{dd,bb}(t_0) \times \\ & \exp\{-X[\omega_2 - \Omega - \langle U(t_0)\rangle - \omega_{dc} - \tilde{K}(t_0)(\omega_1 - \omega_{eg} - \omega_{ba})]^2\} + \\ & G_{cc,aa}(t_0) \exp\{-X[\omega_2 - \omega_{eg} - \omega_{dc} - \tilde{K}(t_0)(\omega_1 - \omega_{eg} - \omega_{ba})]^2\}\}\end{aligned} \tag{7a}$$

$$\omega_{eg} = \Omega + \langle U(0)\rangle \tag{7b}$$

$$X \equiv [W^2 + \Delta^2]/\{2\Delta^2[W^2 + \Delta^2\{1 - K^2(t_0)\}]\} \tag{7c}$$

$$\tilde{K}(t_0) \equiv \Delta^2 K(t_0)/(W^2 + \Delta^2) \tag{7d}$$

The delay time between the peaks of the pump and probe pulses is denoted t_0. μ_{ab} is the transition dipole matrix element of states $|a\rangle$ and $|b\rangle$, and $P(a)$ is the population of state a at thermal equilibrium. Ω is the frequency of the 0–0 transition for the gas-phase solute, and the energy difference of states $|b\rangle$ and $|a\rangle$ is $\hbar(\Omega + \omega_{ba})$. The frequency of the 0–0 absorption transition in the solvated molecule is ω_{eg}, defined in eq 7b. The lifetime of the electronic excited state is taken to be long compared to the experimental time scale. Vibrational relaxation is incorporated through $G_{dd,bb}$ and $G_{cc,aa}$. $G_{jj,nn}(t)$ is the conditional probability that the solute occupies the vibronic state j at time t, if it occupies state n at $t = 0$. In the absence of vibrational relaxation, $G_{jj,nn} = \delta_{jn}$, and when vibrational relaxation is complete, $G_{jj,nn} = P(j)$, the thermal equilibrium population of state $|j\rangle$. In general, $G_{jj,nn}$ may be calculated by postulating a Pauli master equation that describes transitions between vibronic states of the same electronic state.[6] Three further assumptions are made in deriving eq 7. First, Δ is taken to be large compared to the inverse of the time scale of $\langle U(t)\rangle$, which implies that the absorption profile of a single vibronic transition is inhomogeneously broadened. The fact that a vibronic progression of narrow holes was burned in the cresyl violet spectrum at short times indicates that this assumption is valid for the cresyl violet/ethylene glycol system. Second, the overlap of pump and probe pulses is taken to be negligible ($t_0 \geq W^{-1}$). Third, the frequency difference of each pair of ground-state vibronic levels and of each pair of excited-state vibronic levels is taken to be large compared to the inverse of the duration of the pump pulse ($|\omega_{ac}|/W \gg 1$, $|\omega_{bd}|/W \gg 1$).

In order to calculate the differential absorption spectrum from eq 7, we require three quantities associated with the solvent: $\langle U(t)\rangle$, Δ, and $K(t)$. These quantities can be obtained either from an analytical theory or from a molecular dynamics simulation of the solvent, and here we shall adopt the former approach. $\langle U(t)\rangle$ has been calculated for a time-dependent generalization of the Onsager cavity model, by Mazurenko and Bakshiev,[7] Bagchi, Oxtoby and Fleming,[8] and van der Zwan and Hynes,[9] in their investigations of the time-dependent Stokes shift in fluorescence measurements in solution. In this model, the solute is represented by a point dipole located at the center of a spherical cavity of radius a that is surrounded by a dielectric continuum characterized by a dielectric function $\epsilon(\omega)$. The point dipole has a moment μ_g when the solute is in the ground state and has a moment μ_e when the solute is in the excited state. The energy of the system at any time can be related to $\epsilon(\omega)$ by solving Maxwell's equations. Within the Debye model for dielectric response, in which $\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 - i\omega\tau_D)$, $\langle U(t)\rangle$ is given by

$$\begin{aligned}&\langle U(t)\rangle - \langle U(\infty)\rangle = \\ &6(\mu_e - \mu_g)^2 a^{-3}\{(\epsilon_0 - \epsilon_\infty)/[(2\epsilon_0 + 1)(2\epsilon_\infty + 1)]\} \exp(-t/\tau_s)\end{aligned} \tag{8a}$$

$$\langle U(\infty)\rangle = -\mu_e\cdot(\mu_e - \mu_g)[2(\epsilon_0 - 1)]/[a^3(2\epsilon_0 + 1)] \tag{8b}$$

$$\tau_s \equiv \tau_D(2\epsilon_\infty + 1)/(2\epsilon_0 + 1) \tag{8c}$$

The characteristic time scale of $\langle U(t)\rangle$ is the solvation time τ_s, which is related to the Debye dielectric relaxation time τ_D in eq 8c. The solvation time is very similar in magnitude to the longitudinal relaxation of the dielectric medium,[10] which is usually defined to be $\tau_D\epsilon_\infty/\epsilon_0$. As $U(t)$ is taken to be a Gaussian variable, $\langle \delta U(t)\delta U(0)\rangle$ can be calculated from $\langle U(t)\rangle$ with a fluctuation dissipation relation.[4,11] In the high-temperature limit, we have

$$\langle \delta U(t)\delta U(0)\rangle = kT[\langle U(t)\rangle - \langle U(\infty)\rangle] \tag{9}$$

Equations 4, 8, and 9 give $\langle U(t)\rangle$, Δ, and $K(t)$ in terms of the solute radius and dipole moments and the dielectric properties of the solvent. The differential absorption spectrum may now be calculated by substituting eq 8 and 9 into eq 7.

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In eq 7, $\Delta\alpha$ is expressed as the sum of two terms. The first term, which contains $G_{dd,bb}$, reflects dynamics of molecules that are electronically excited at the time of probing, while the second term, which contains $G_{cc,aa}$, reflects dynamics of molecules in the ground state. Since the absorption spectrum is proportional to the population difference between the ground and excited electronic states, both ground-state and excited-state dynamics enter into $\Delta\alpha$. The primary difference between hole-burning spectroscopy (as well as other forms of four-wave mixing[3,12]) and spontaneous fluorescence measurements is that the former techniques can probe both ground- and excited-state dynamics, while the latter experiment probes only dynamics in the excited state. The first term in eq 7 has the same time and frequency dependence as an expression recently derived by us for the fluorescence spectrum at ω_2 measured at a time t_0 following the application of an excitation pulse with central frequency ω_1.[4] Examination of this term reveals that at short times, there will be a sequence of narrow holes when $\hbar(\omega_2 - \omega_1)$ is approximately equal to the energy difference of two vibronic states of the ground-state manifold. As the solvent relaxes about the dipole of the electronically excited solute, these holes broaden and undergo a red-shift. At long times, this first term is proportional to the steady-state fluorescence spectrum of the solute. At short times, the second term adds a sequence of narrow holes when $\hbar(\omega_2 - \omega_1)$ is approximately equal to the energy difference of two vibronic states of the excited-state manifold. For delay times that are long compared to the solvation time ($K(t_0) \ll 1$) and that are long on the time scale of vibrational relaxation ($G_{cc,aa}(t_0) \cong P(c)$), this term factors into the product of the unperturbed absorption spectrum at ω_1 and the unperturbed absorption spectrum at ω_2. The holes contributed by this second term broaden in time and will undergo a red shift for $\omega_1 > \omega_{eg}$ or a blue shift for $\omega_1 < \omega_{eg}$. For $\omega_1 = \omega_{eg}$, these holes broaden but do not shift. Equation 7 shows that vibrational relaxation within a single vibrational mode can alter the magnitudes of the vibronic holes, or, if the mode has different frequencies in the ground and excited electronic states, can cause the appearance of new holes. Vibrational relaxation within one mode does not lead to line broadening or to a continuous spectral shift. By contrast, vibrational relaxation from one optically active mode to a large number of dark modes whose frequencies in the ground and electronic excited states are slightly different can lead to line broadening.[6] *However, solvent reorganization alone may account for the line broadening and continuous red shift observed by Shank and co-workers.*

The measurements of Shank et al. indicate that significant solvation may occur in 100 fs in ethylene glycol at room temperature. Quantitative application of eq 7 to the cresyl violet experiments requires knowledge of the dielectric relaxation in ethylene glycol on the picosecond and femtosecond time scales. The dielectric relaxation of ethylene glycol is well characterized for frequencies up to 100 GHz,[13] but data for shorter time scales is not currently available. Figure 2 shows $\Delta\alpha$ calculated from eq 7 for a model solute in ethanol at 247 K. The dielectric parameters for ethanol at 247 K are $\epsilon_0 = 33.5$, $\epsilon_\infty = 4.8$, and $\tau_D = 1.05$ ns.[14] According to eq 8c, the solvation time τ_s is 164 ps. We take $\omega_1 = \omega_{eg}$. The pump pulse has a full width at half maximum of 1 ps. The model solute has a single optically active, harmonic vibration whose frequency in the ground and excited electronic states is 590 cm^{-1}. $|\mu_e - \mu_g| = 6$ D. The equilibrium value of the vibrational coordinate changes by $0.75\ (\hbar/m\omega')^{1/2}$ upon electronic excitation, where m is the reduced mass and ω' is the vibrational frequency (a dimensionless displacement of 0.75). The solute has an effective radius of $a = 3$ Å. *Vibrational relaxation is not included in the calculations shown in Figure 2.* The top frame in Figure 2 shows the unperturbed absorption spectrum (no pump pulse) for the model system. The following frames show $\Delta\alpha$ measured at a sequence of delay times between the pump and probe pulses. For $t_0 \ll \tau_L$, $\Delta\alpha$ consists of a progression of sharp lines, separated by the vibrational frequency, as was observed in the cresyl violet experiments. At longer times, these vibronic holes broaden and undergo a red shift. The dashed curve in the lowest frame shows the asymptotic behavior of $\Delta\alpha$ for t_0 much greater than τ_L but still small compared to the excited-state lifetime. For such long times, $\Delta\alpha$ is composed of two broad holes, which arise from the two terms in eq 7. The principal difference between Figure 2 and the cresyl violet data (Figure 2 of ref 1a) lies in the relative time scales of the line broadening and the line shift. In Figure 2, the broadening occurs rapidly on the time scale of the shift, while the experimental data show a shift and a broadening that occur on comparable time scales. The separation of time scales between broadening and shift in the present calculation is primarily a consequence of eq 9, in which the broadening and shift are related by a high-temperature fluctuation–dissipation theorem. Comparison of Figure 2 to Figure 2 of ref 1a indicates that the simple relationship in eq 9 may not be accurate for cresyl violet in ethylene glycol at room temperature. More sophisticated calculations of $\langle U(t)\rangle$ and $\langle\delta U(t)\delta U\rangle$, from simulations for example, together with eq 7, which relates these quantities to the experimental observable, may yield results that are in better quantitative agreement with the experiment.

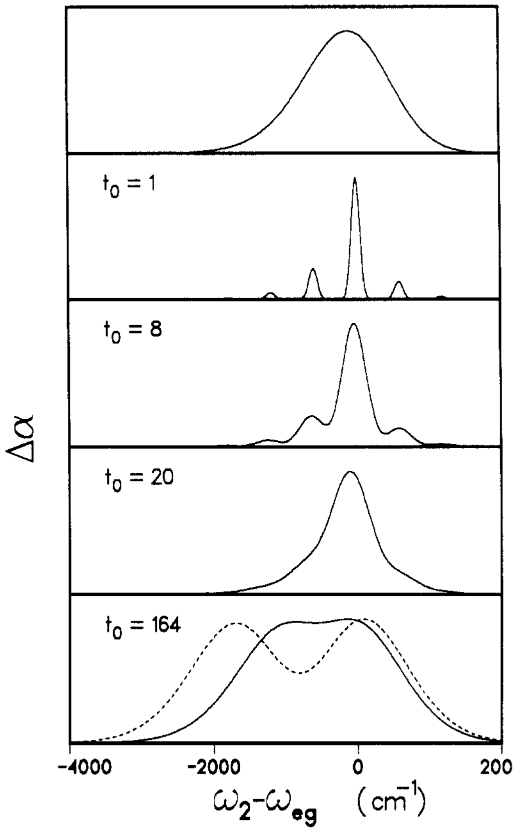

Figure 2. The top frame shows the unperturbed absorption spectrum of a model solute with a harmonic vibration at 590 cm^{-1} with a dimensionless displacement of 0.75 in ethanol at 247 K. $\omega_1 = \omega_{eg}$. The solute dipole moment changes by 6 D upon excitation, and the effective radius of the solute is $a = 3$ Å. The following frames show the differential absorption spectrum $\Delta\alpha$ for successively longer delays between the probe pulse and the 1-ps pump pulse. Each spectrum is labeled with the delay time t_0 in picoseconds. The solvation time τ_S is 164 ps. The dashed curve in the lowest frame shows $\Delta\alpha$ for $t_0 \gg \tau_S$. Vibrational relaxation is not included.

There is currently considerable interest in using time-resolved fluorescence measurements to probe solvation dynamics.[15-18] Such

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measurements may not be practical on time scales that are 1 or 2 orders of magnitude smaller than the solute fluorescence lifetime. Our analysis shows that hole-burning spectroscopy provides a direct probe of solvation dynamics on a time scale that is limited only by the durations of the pump and probe pulses.

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Time-Resolved Emission at the Glass-to-Fluid Transition. Localization or Delocalization in Polypyridyl-Based Metal-to-Ligand Charge-Transfer Excited States of Ruthenium and Osmium?

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The time dependence of MLCT excited-state emission for [Os(phen)(das)$_2$]$^{2+}$ in the glass-to-fluid transition region in 4:1 ethanol–methanol is analogous to that observed earlier for [Ru(bpy)$_3$]$^{2+}$. This observation calls into question the earlier suggestion that the origin of the time dependence in the emission spectrum of Ru(bpy)$_3$$^{2+}$ is a delocalized, [Ru(bpy$^{-1/3}$)$_3$]$^{2+*}$, to localized, [(bpy)$_2$Ru(bpy$^-$)]$^{2+*}$, transition. In the osmium complex the time-dependent shifts to lower energy are proposed to arise from a dynamic solvent effect involving solvent dipole reorientations.

Introduction

Although they are well studied,[1] an apparent controversy exists in the description of the luminescent metal-to-ligand charge-transfer (MLCT) excited states of polypyridyl complexes of Ru(II) and Os(II). The controversy arises in multiple chelates like Ru(bpy)$_3$$^{2+}$ (bpy is 2,2′-bipyridine) where a question exists as to whether the excited electron is localized on a single bpy ligand, [(bpy)$_2$Ru^{III}(bpy$^-$)]$^{2+*}$, or is delocalized over all three, [Ru^{III}(bpy$^{-1/3}$)$_3$]$^{2+*}$. The experimental evidence in fluid solution is consistent with localization in the excited state[2–6] while results obtained in the solid state have remained somewhat equivocal.[7] In a recent experiment a time dependence observed in the emission spectrum of Ru(bpy)$_3$$^{2+}$ near the glass transition region in 4:1 (v/v) ethanol–methanol was attributed to a transition between delocalized and localized MLCT states.[8] We report here that a very similar effect is observed for the *mono*-polypyridyl complex [Os(phen)(das)$_2$](PF$_6$)$_2$ (das is 1,2-dimethylarsinobenzene; phen is 1,10-phenanthroline) where there is no ambiguity concerning the orbital basis of the acceptor levels for the excited electron since there is only a *single* chromophoric ligand. For the osmium complex we attribute the temporal effect to a dynamic reorientation of solvent dipoles in response to the change in electronic structure between the ground and excited states which calls into question the existence of a delocalized to localized transition for Ru(bpy)$_3$$^{2+}$.

Experimental Section

The synthesis and purification of the osmium complexes have been reported elsewhere.[9] Spectroscopic grade ethanol and methanol were singly distilled and stored over molecular sieves under nitrogen. Samples for emission studies were freeze–pump–thaw degassed at <10^{-5} Torr for at least five cycles and sealed under vacuum. Temperature control was maintained by a Janis Research NDT cryostat and a Lake Shore Cryogenic DRC84C controller. Steady-state emission spectra were recorded with an SLM Instruments Series 8000 photon-counting spectrofluorimeter corrected for instrumental response. Time-resolved emission spectra were obtained with a 0.25-m monochromator, a Hamamatsu R446 P.M.T., and a Tektronix 7912AD transient digitizer interfaced to a PDP 11/34 minicomputer. The 337-nm fundamental of a Molectron UV400 nitrogen laser (pulse width ~ 5–8 ns at 50 μJ per pulse) was used for right angle excitation with a nitromethane filter to remove scattered laser light.

Results

Temperature-dependent, steady-state emission spectra for the complex [Os(phen)(das)$_2$](PF$_6$)$_2$ are shown in Figure 1. At temperatures near the glass transition region there is a marked blue shift of the maximum accompanied by the appearance of a well-defined vibrational structure. The significant shift to higher energy with decreasing temperature appears to be a general phenomenon for many organic[10] and MLCT excited states[11] where there is significant charge-transfer character to the excited state. Recently, based on temperature-dependent emission and lifetime

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