A U-shaped Arrhenius behaviour for emission decay: temperature-dependent switching between excited-state decay paths

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Temperature variation causes a switching between excited-state decay paths to give a U-shaped Arrhenius plot.

The photophysical properties of ruthenium tris(diimine) complexes are well understood.[1] As such, they can be used to study how various environmental factors can be used to modulate photochemical processes.[2] It has been well established that photoexcitation of typical ruthenium polypyridyl complexes generates a singlet metal-to-ligand charge-transfer state (^{1}MLCT) which undergoes efficient intersystem crossing to a manifold of closely spaced triplet states (^{3}MLCT). As shown in Fig. 1, these states can then decay back to the ground state through both radiative (k_r) and non-radiative (k_{nr}) mechanisms, in addition to a thermal population of high-lying ligand field states (^{3}LF).[1,3] Thus, the emission lifetimes of most ruthenium tris(diimine) complexes generally decrease with increasing temperature in fluid solution. In such cases energy gaps of ΔE = 2500–4100 cm^{-1} have been reported to separate the ^{3}MLCT and ^{3}LF states.[4]

In recent work, we reported strong solvatochromic behavior in the emission properties of a novel ruthenium polypyridyl complex, [Ru^{II}(bpy)$_2$L], where L is a non-symmetrically substituted 2,2′-bipyridyl ligand having two carboxylate groups located at one of its two pyridyl rings: L = 3,5-dicarboxy-2,2′-bipyridine.[5] When dissolved in acetonitrile, this compound behaves much like [Ru^{II}(bpy)$_3$], having an emission maximum at λ_{em} = 637 nm, a lifetime of τ = 846 ± 11 ns (295 K), and decay rates (k_{obs} = 1/τ) that follow a thermally activated behaviour in which E_a = + 4170 ± 200 cm^{-1}. In contrast, when [Ru^{II}(bpy)$_2$L] is dissolved in water its emission spectrum becomes strongly red-shifted (λ_{em} = 685 nm at 295 K) corresponding to a solvent stabilization of its ^{3}MLCT states by *ca.* 1100 cm^{-1}. The strongly red-shifted emission predicts that (*i*) the excited-state lifetimes in water would be very small as dictated by the energy-gap law,[6] and (*ii*) thermal access to the deactivating ^{3}LF would be severely diminished at ambient temperatures. The excited-state lifetimes of [Ru^{II}(bpy)$_2$L] in water are indeed very short (τ = 54 ± 1 ns at 280 K) and follow an unusual temperature dependence by *increasing* with increasing temperature throughout the accessible temperature range, to τ = 75 ± 1 ns at 360 K. The corresponding decay rates can be fit to the Arrhenius expression to give a small, negative activation energy for emission decay of E_a = −270 ± 15 cm^{-1} (Fig. 2). These results showed that solvatochromic shifts in emission can be used to alter the emission energies of [Ru^{II}(bpy)$_2$L] to produce a solvent-dependent switching between different excited-state deactivation paths. In the present communication, we report that temperature variation can also be used to systematically tune the emission energies of this compound to yield a novel *temperature-dependent* switching between emission decay paths.

When [Ru^{II}(bpy)$_2$L] is dissolved in methanol, an unusual temperature dependence of k_{obs} can be seen (Fig. 2). At low temperatures (≤305 K), the decay rates display negatively activated behaviour similar to that previously seen in water. Within this regime, the emission lifetimes increase with increasing temperature from τ = 187 ± 3 ns at 205 K to τ = 368 ± 4 ns at 305 K.

A fit of the emission decay rates to eqn. (1) yields A = 6.5

$$k_{obs} = A\exp(-E_a/RT) \qquad (1)$$

± 0.3 × 10^5 s^{-1} and E_a = −300 ± 15 cm^{-1}, which is nearly identical to the activation energy reported in water. Experiments

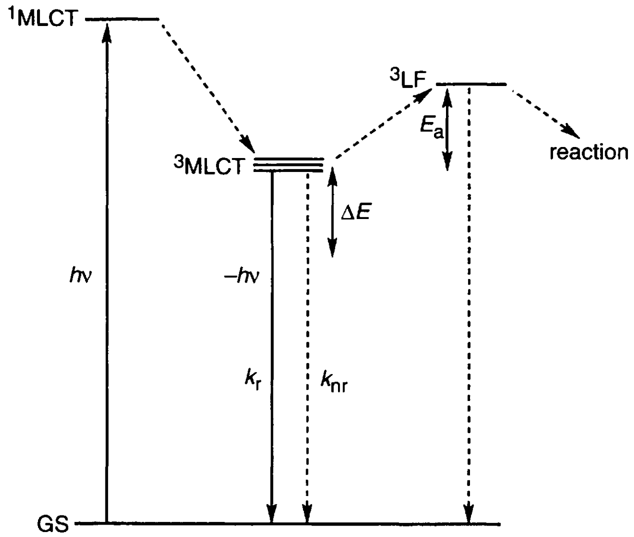

Fig. 1 Energy-level diagram showing the excited-state processes occurring in ruthenium polypyridyl compounds. ΔE reflects the variation in emission energies that can arise in response to changes in solvent and/or temperature.

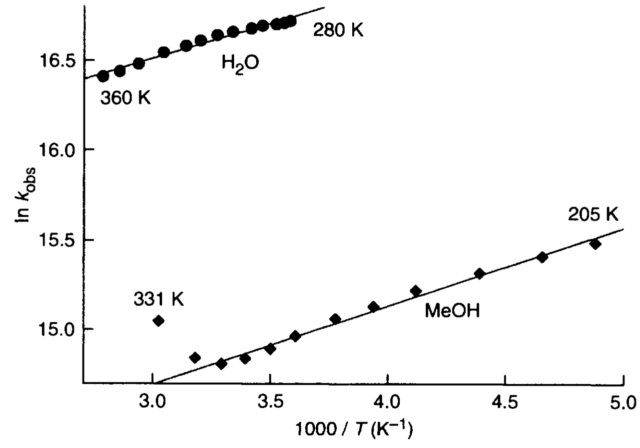

Fig. 2 Plot of ln k_{obs} *vs.* 1/T taken in water and methanol. The solid lines are from fits of the data as described in the text (T = 280–360 K in water, T = 205–305 K in methanol). Error bars are smaller than the symbols.

performed in CD_3OD show qualitatively similar behaviour but one in which the observed activation energy is of lower magnitude, $E_a = -200 \pm 10$ cm^{-1}. The observed solvent isotope effect suggests that specific solute–solvent interactions may play an important role in determining the mechanisms for the negative activation energy.† A markedly different temperature dependence of k_{obs} is seen from the data obtained at high temperatures (> 305 K). Here, emission lifetimes begin to decrease with increasing temperature in a manner similar to that reported in acetonitrile. From the limited data obtained within this regime, a fit to a modified Arrhenius expression[3] [eqn. (2)] yields $k_0 = 2.6 \times 10^6$ s^{-1}, $A = 1.7 \times 10^{15}$ s^{-1}, and $E_a = +4900$ cm^{-1}.

$$k_{obs} = k_0 + A\exp(-E_a/RT) \qquad (2)$$

To better determine the role of temperature in governing the magnitude of k_{obs} in methanol, temperature-dependent emission spectra were obtained. At 295 K, the emission maximum occurs at $\lambda_{em} = 652$ nm, which is intermediate between the values previously observed in acetonitrile and water. However, this emission is strongly thermochromic, showing a shift to higher energies upon increasing temperatures (Fig. 3, inset). It is significant to note that the low temperature maxima ($\lambda_{em} = 668$ nm at 220 K) are similar to those previously observed in water. At high temperatures the maxima ($\lambda_{em} = 642$ nm at 328 K) are nearly identical to that seen in acetonitrile at 295 K. Thus, temperature variation has the effect of tuning the emission energies of [Ru^{II}(bpy)$_2$L] between the two limiting energy regimes previously reported.[5]

As shown in Fig. 2, the demarcation between the regions of normally and negatively activated behaviour occurs at 305 K. It is therefore important to characterize the nature of the excited-state decay processes that occur both above and below this temperature. The energy-gap law for radiationless transitions states that the rates of non-radiative decay (k_{nr}) should vary exponentially with emission energy (E_{em}) according to eqn. (3),[6] where $k_{nr} = [k_{obs} - k_r]$, $k_r = [\phi/\tau_{obs}]$, ϕ is the emission

$$\ln k_{nr} = A - BE_{em} \qquad (3)$$

quantum yield, and A and B are constants. Thus, the thermochromic emission behaviour discussed above predicts that a linear relationship should exist between $\ln k_{nr}$ and the temperature-induced variation in E_{em}. As seen in Fig. 3, the predicted behaviour is precisely that shown for data obtained within the low-temperature regime ($T \leqslant 305$ K). These results demonstrate that the negatively activated rates of emission decay can be explained in terms of a temperature-induced energy-gap law behaviour occurring at low temperatures. In contrast, the non-radiative decay rates obtained at higher temperatures ($T > 305$ K) clearly deviate from this trend. The apparent enhancement of k_{nr} over those predicted by the energy-gap law is consistent with a change in deactivation paths to one that involves an enhanced thermal access to the deactivating ^{3}LF states, as determined by the temperature dependence of k_{obs}.

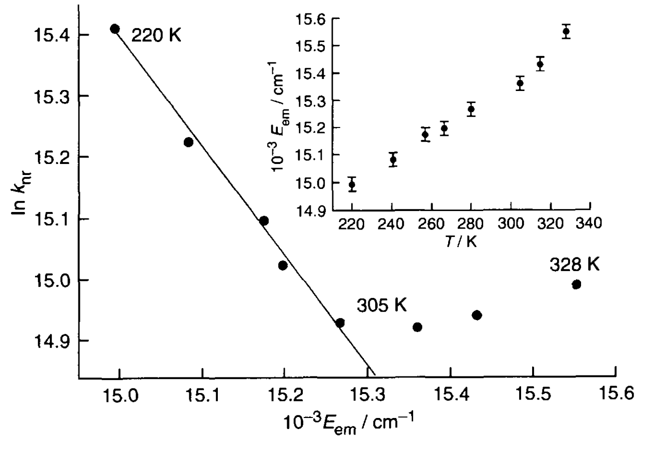

Fig. 3 Plot of ln k_{nr} *vs.* E_{em} taken in methanol. Linear behaviour predicted by eqn. (3) is observed for $T < 305$ K suggesting that temperature-induced energy-gap law behaviour is obtained. Deviations from linearity occur at higher temperatures. Inset: Variation of emission energy with temperature.

In summary, an unusual U-shaped Arrhenius curve has been observed for the emission decay rates of [Ru^{II}(bpy)$_2$L]. Thermochromic and temperature-induced energy-gap law data have been used to suggest that such behaviour results from a temperature-induced switching between different excited-state decay paths. These results demonstrate the importance of considering specific solvation effects in the study of unusual temperature behaviour in the excited-state lifetimes of this and related[4,7] compounds.

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Footnote

† The formation of intermolecular hydrogen bonds to solvent is known to play an important role in the emission quenching of both organic[8] and inorganic complexes.[9] However, to our knowledge, the thermal regulation of such interactions has not been previously reported to produce negatively activated processes.

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