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Solvent Relaxation and Intersystem Crossing in Trisethylenediaminechromium(III)

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The role of solvent in non-radiative processes between electronic states of transition metal complexes has been a question of some interest [1, 2]. In particular, the relationship of solvent relaxation to the intersystem crossing efficiency (ϕ_{ISC}) in $Cr(en)_3^{3+}$ has been discussed [3]. The issue is this: is intersystem crossing ($^4T_2 \rightsquigarrow {}^2E$) so fast that solvent molecules cannot move sufficiently to permit the complex in the $^4T_2$ state to relax to an equilibrium geometry? Kane-Maguire, *et al.* [3] argue that solvent relaxation is unimportant in this case. We now present evidence that points to the importance of solvent restriction in the $Cr(en)_3^{3+}$ $^4T_2 \rightsquigarrow {}^2E$ process.

$Cr(en)_3^{3+}$ in water and in a mixed aqueous solvent containing 80% glycerol (V/V) was excited by an N_2 laser (337 nm) or an N_2 pumped dye laser. The decay curves were plotted semilogarithmically and extrapolated to t = 0. The resultant intensity (I(o)) is a measure of $\phi_{ISC}k_{rad}$ [4] where k_{rad} is the $^2E \rightarrow {}^4A_2$ radiative rate. Highly concentrated solutions were used and the emission emanated from essentially a point source. The angle between the excitation and emission was 45°. Under these conditions the change in I(o) due to refractive index variations is small [5] and no refractive index corrections were applied.

The dependence of I(o) upon excitation wavelength is shown in Fig. 1 for aqueous solutions. These quantities were calculated after correction for the variation in the incident light intensity by means of a Rhodamine B quantum counter. Since τ is independent of excitation wavelength, the I(o) behavior is a direct measure of the phosphorescence quantum yield variation, and the results are in accord with those reported by Kane-Maguire, *et al.* In Fig. 2, the ratios of I(o) in 80% glycerol–water to that in water are presented. The change in lamp output with wavelength is of no consequence for the determination of these ratios. The optical densities were the same in both solutions. Except for the small refractive index effect, the ratios are free from systematic error. If the refractive index corrections were applied, I(o) would be the same in both solutions when λ_{exc} = 337 nm.

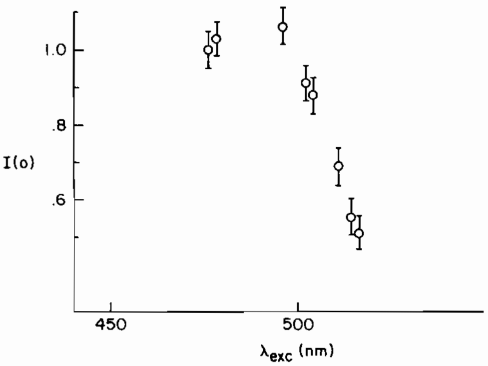

Fig. 1. I(o) dependence upon excitation wavelength for $Cr(en)_3^{3+}$ in water.

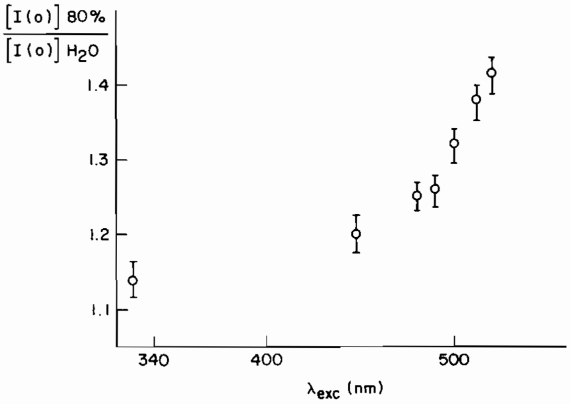

Fig. 2. The ratio of $Cr(en)_3^{3+}$ I(o) in 80% glycerol–water (V/V) and water.

The data in Figs. 1 and 2 can be combined to yield the I(o) dependence on λ_{exc} in the viscous solvent. Clearly, *as the viscosity is increased the change in I(o) with wavelength is decreased.* Whatever the source of the different I(o) behavior in the two solvents, it does appear that any analysis of this effect must include solvent relaxation. We would predict, in a rigid glass medium, a ϕ_{ISC} that is not dependent on λ_{exc}.

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