

Early picosecond photophysical dynamics and vibrational energy relaxation in Ru(II)polypyridyl complexes

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Introduction.

The light-switch properties of the DNA-intercalating complex, $[\text{Ru}(\text{phen})_2(\text{dppz})]^{2+}$ (where dppz is dipyridophenazine) have stimulated extensive investigations of its photophysical properties, primarily due to the presence of several low lying excited states of similar energy. Recent work has shown that solvent co-ordination and relaxation are involved in controlling the relative rates of radiative and non-radiative relaxation. Our earlier resonance Raman studies¹⁾ of this complex supported a previously proposed^{2a)} three state model (subsequently extended^{2b,c)} to explain the solvent-dependent excited state dynamics. During the course of these studies, however, several observations prompted us to re-examine the early picosecond photophysics associated with $[\text{Ru}(\text{bpy})_3]^{2+}$. $[\text{Ru}(\text{bpy})_3]^{2+}$ has long been regarded as a paradigm species with respect to the spectroscopy and photophysics of transition metal complexes⁴⁾ and continues to be the subject of further publications⁵⁾. Until relatively recently the majority of these studies have focused on the lowest thermally equilibrated excited (THEXI) states (i.e. ³MLCT manifold). Over the last decade, advances in laser technology and analytical techniques have lead to a resurgence of interest in complexes that were previously considered to be fully understood. The processes which occur in the time interval between excitation to the Frank-Condon state and relaxation to the THEXI states, have received an increasing amount of attention³⁾, not least due to the recognition that significant photochemical processes such as charge injection in photovoltaic cells⁶⁾ and energy transfer in multinuclear complexes can occur via states lying higher than the THEXI states⁷⁾. Understanding the factors, which influence these early processes is clearly of significance with regard to the extent of control over the formation of long-lived charge-separated species.

Results and Discussion

In our earlier contribution^{3a)} we reported the presence of a high energy emission ($\lambda_{\text{max}} = 520 \text{ nm}$) from $[\text{Ru}(\text{bpy})_3]^{2+}$ which was seen to decay within $<3 \text{ ps}$. We also observed an increase in the lifetime of this emission to times beyond 200 ps, upon deuteration of the bpy ligands. Although, our more recent studies^{8a)} have confirmed that the rapidly decaying ($<3 \text{ ps}$) emission at 520nm does arise from $[\text{Ru}(\text{bpy})_3]^{2+}$, we have since concluded that the effect of deuteration is not related to an increase in the lifetime of the 520 nm emission. Extensive studies have been carried out to establish the cause of this deuteration effect, and although emission from free ligand has been ruled out as the source^{8a)}, we have been unable to establish definitely the origin of the longer-lived emission. Interestingly, in recent work McFarlane *et al.*^{8b)} have also noted the observation of a similar 'unidentified' emission, with a lifetime comparable to that observed by us.

During the present reporting period a series of picosecond time resolved resonance Raman (TR³) experiments was carried out at the USL to examine the effect of solvent on the vibrational structure of $[\text{Ru}(\text{bpy})_3]^{2+}$ and its isotopologues. A summary of the findings is presented here. Figure 1 shows an example of the

spectra obtained for the pure excited state complex after solvent and ground state (-20ps) spectral subtractions. A noteworthy feature here is the grow-in of the characteristic band of the ³MLCT excited state at 1475 cm^{-1} .

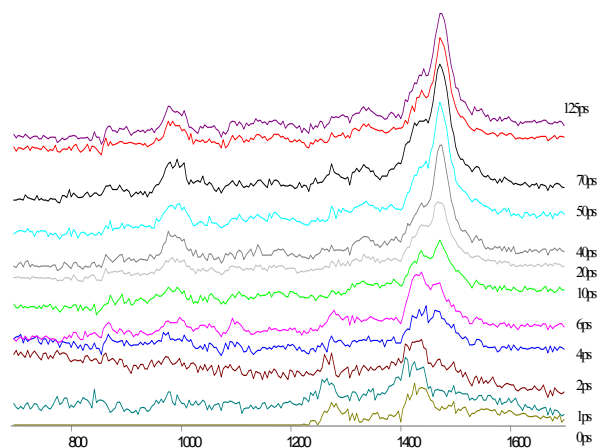


Figure 1. Time Resolved Excited State Resonance Raman of $[\text{Ru}(\text{bpy})_3]^{2+}$ in 1-hexanol; Pump at 400nm, Probe at 475nm.

The kinetics of the grow-in of the 1475 cm^{-1} band are shown in Figure 2. The insert shows the kinetics observed for the first 80 ps. The growth of the band at 1475 cm^{-1} is essentially complete within 50 ps. The band apparent at 1428 cm^{-1} , which reaches a maximum at about 25 ps, is due to solvent. Figure 3 shows the comparison of the kinetics in various solvents. It is apparent that over a series of alcoholic solvents the rise time of this signal is approximately constant despite the very different viscosities and dielectric constants.

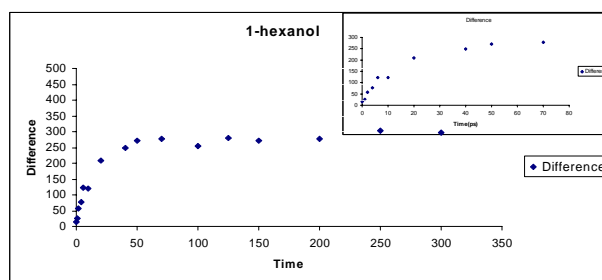


Figure 2. Kinetics of Excited State Formation at 1475 cm^{-1} in 1-hexanol. Inset shows the kinetics for the first 80 ps.

Similarly, the effect of counter-ion on the early photophysics was investigated. $[\text{Ru}(\text{bpy})_3]^{2+}$ was prepared with chloride, hexafluorophosphate and tetrakis(3,5-di(trifluoromethyl)-phenyl)borate (BARF) counterion. Again no counter-ion dependence was observed on the kinetics of the grow-in of the ³MLCT state. The results suggest that significant ion-pairing effects are not implicated in the

processes observed. In addition, the difference in kinetics between the ultrafast emission at 520 nm (<3 ps) and the relatively slow rise in the ³MLCT (THEXI) state confirm that the effects are due to distinct processes. The results point to a need for revision of suggestions that the relaxation to the thermally equilibrated ³MLCT state occurs on the femtosecond timescale.

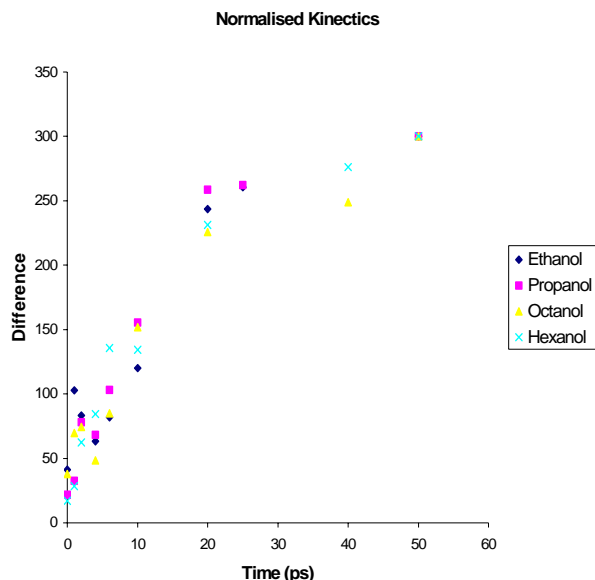


Figure 3. Kinetics of 1475 cm⁻¹ band in Ethanol, Propan-o-l Octan-1-ol and Hexan-1-ol.

In order to examine further the equilibration of the ³MLCT state, anti-Stokes measurements (λ_{pump} 400 nm, λ_{probe} 475 nm) were attempted. However, a practical problem due to the overlap of the Stokes bands from the pump beam with the anti-Stokes bands from the probe precluded observation of the weak anti-Stokes bands. Anti-Stokes measurements were also attempted with λ_{pump} at 265 nm and λ_{probe} at 400 nm, however, Stokes radiation from the pump beam again dominated the spectra.

Conclusion.

We and others^{3,8)} have confirmed the observation of a < 3ps high energy emission from [Ru(bpy)₃]²⁺ initially observed directly in fluorescence upconversion measurements by Bhasikuttan *et al.*^{3d)} The present studies demonstrate that the THEXI (³MLCT) state evolves over a much longer timescale (persisting to ~ 20 ps) than previously supposed. It is clear that, although there have been great strides in the understanding of [Ru(bpy)₃]²⁺ photophysics, there remain some unresolved questions, open to further investigation on picosecond and femtosecond timescales.

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