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L.A. Philips, W.T. Brown, S.P. Webb,
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Picosecond Time-Resolved Spectroscopy of Electronically Excited tris(2,2'-bipyridine)Ruthenium(II) Dichloride

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1. Introduction

Transition metal complexes display a rich and varied photochemistry which has found broad application in such areas as solar energy conversion, electron transfer reactions, and lasers[1-4]. Although tris(2,2'-bipyridine)ruthenium(II) dichloride ($\text{Ru}(\text{bpy})_3^{2+}$) has been extensively studied[4-10], many details of its excited-state dynamics remain unresolved. The lowest charge-transfer excited state of $\text{Ru}(\text{bpy})_3^{2+}$ has been the focus of some controversy. CROSBY and others [6-8] have established that initial excitation occurs via a $d \rightarrow \pi^*$ transition. Assignment of the state(s) involved in subsequent energy transfer and emission remain in question. LYTLE and HERCULES suggested a two-state model, as shown in Fig. 1[6]. In this model energy transfer occurs via rapid radiationless relaxation ($A \rightarrow B$), but emission occurs from both states at times short compared to τ_{AB} . At longer times emission occurs only from state B. CROSBY suggested an alternative model involving three closely spaced mixed states[9,10]. In this model, room temperature emission occurs predominately from one of these three states. Once it is formed, the emitting state has been shown to have a lifetime of 600 ns in aqueous solution at room temperature[6].

WOODRUFF et al.[5] demonstrated that the emitting state is formed in less than 7 ns using time-resolved resonance Raman spectroscopy (TR^3) of the excited state. With a time resolution limited to 7 ns, it was not possible to observe the dynamics of the energy transfer between the initially excited state and the emitting state. In the present study, picosecond TR^3 and time-resolved emission spectroscopy have been used in an attempt to answer some of these questions surrounding the dynamics of the excited state formation and decay.

2. Experimental

In both experiments the excitation source was an amplified single pulse selected from the pulse train of a passively mode-locked Nd:YAG laser (Quantel, YG400). The third harmonic at 355 nm was used to excite the $\text{Ru}(\text{bpy})_3^{2+}$. In the time-resolved emission experiments, the luminescence was imaged onto the photocathode of an ultrafast streak camera (Hadland Photonics, IMACON 500) at a right angle to the excitation beam. A fiducial pulse which accompanied the luminescence acted as a time reference and provided a monitor of the quality of the excitation pulse. Typical excitation pulses were 23 ± 7 ps in duration with an energy of ~ 100 μJ . The signal from the streak camera was imaged onto a diode array (Tracor-Northern, IDARSS) and read off the array into an LSI 11/2 computer. The computer evaluated each laser shot and signal averaged the accepted data.

Fig. 1 Two-state kinetic model for electronically excited $\text{Ru}(\text{bpy})_3^{2+}$, from LYTLE and HERCULES[6]

In the Raman experiments, a single 355 nm pulse was used both to excite ground state molecules and to induce resonance Raman scattering from excited molecules. The Raman signal was imaged into a double monochromator (Spex, Model 1404) and was detected by a photomultiplier tube (RCA, 1P28). The output of the photomultiplier was sent through a gated integrator (Evans Assoc., Model 4130) and into an LSI 11/2 computer. The computer averaged the signal from 500 shots at each spectral point and scanned the monochromator. The picosecond resonance Raman spectra were taken at a resolution of 14 cm^{-1} . $\text{Ru}(\text{bpy})_3^{2+}$ (Strem) was used without further purification. Solutions were prepared in 1.0 M aqueous Na_2SO_4 at $\text{Ru}(\text{bpy})_3^{2+}$ concentrations of 10^{-3} to 10^{-5} M.

3. Results and Discussion

Figure 2 shows the TR^3 spectrum taken with 25 ps pulses in comparison with WOODRUFF's results using 7 ns pulses. Apparent differences in the baselines are due to instrumental effects. WOODRUFF et al. have argued that the TR^3 spectrum they observe is due to the emitting state[5]. The picosecond TR^3 spectrum suggests that the state WOODRUFF is probing at 7 ns is formed in less than 25 ps. Although there is no evidence of a separate, initially excited state in the picosecond TR^3 spectrum, the presence of another state cannot be completely ruled out. Multiple mixed states may have similar Raman spectra which are not distinguishable with the available sensitivity and resolution of the picosecond TR^3 apparatus.

The results of picosecond, time-resolved emission experiments provide additional information about the excited-state dynamics of the $\text{Ru}(\text{bpy})_3^{2+}$ system. The onset of luminescence is prompt, with a risetime of < 5 ps. Using the rate constants of the LYTLE and HERCULES analysis[6], one would predict that both luminescence from the initially excited state (A) as well as from the final emitting state (B) would be observed. LYTLE and HERCULES estimate the rate of transfer from A to B to be on the order of 10 ps or less. Figure 3 shows the experimental data and two calculated curves. Curve I is a single exponential fit to the data with a risetime of < 5 ps. Curve II is a fit calculated using the LYTLE and HERCULES model assuming a τ_{AB} of 1 ps. The LYTLE and HERCULES model does not accurately represent the data. In contrast, a single exponential description of the data is consistent with the CROSBY model. The results of these experiments call into question the existence of any short-lived emitting states in the luminescence of $\text{Ru}(\text{bpy})_3^{2+}$.

Fig. 2 Time-resolved resonance Raman spectra of electronically excited $\text{Ru}(\text{bpy})_3^{2+}$. Upper trace taken with a pulse duration of 25 ps. Lower trace taken with a pulse duration of 7 ns[5]. The excitation wavelength was 355 nm in both cases

Fig. 3 Time-resolved emission from electronically excited $\text{Ru}(\text{bpy})_3^{2+}$. Experimental data and two computer-generated fits are plotted. Fit I shows a single exponential rise of <5 ps. Fit II is a multiple exponential fit based on the model of [6]

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