

Application of Transient Infrared Spectroscopy to Intramolecular Energy Transfer in $[(\text{phen})(\text{CO})_3\text{Re}^{\text{I}}(\text{NC})\text{Ru}^{\text{II}}(\text{CN})(\text{bpy})_2]^+$

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Significant advances have been made in the design and characterization of molecular assemblies which, when photolyzed, undergo intramolecular electron or energy transfer.² These reactions have typically been followed with use of transient electronic spectroscopy. This technique, however, suffers from the disadvantage that absorption bands tend to be broad and featureless, which can lead to ambiguous interpretations, especially where there is more than one absorbing chromophore. Time-resolved resonance Raman spectroscopy has been successfully applied to the study of excited states and molecular assemblies,^{3–6} but time-resolved infrared spectroscopy is particularly well-suited for complexes containing ligands such as CO or CN.^{7,8} Unlike the transient Raman experiment, infrared spectroscopy does not rely on resonance enhancement in the excited state since the

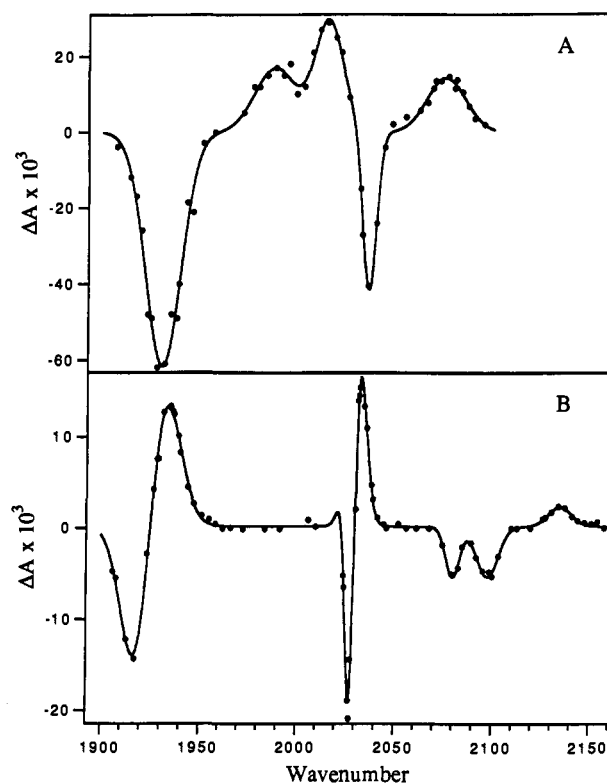


Figure 1. (A) Transient infrared absorption difference (ΔA) spectrum 150 ns after 354.7 nm excitation ($\sim 250 \mu\text{J}$ per pulse) of *fac*- $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(4\text{-Etpy})]^+$, 1 mM, in acetonitrile at room temperature. (B) Transient spectrum 200 ns after 354.7-nm excitation of $[(\text{phen})(\text{CO})_3\text{Re}^{\text{I}}(\text{NC})\text{Ru}^{\text{II}}(\text{CN})(\text{bpy})_2]^+$ in acetonitrile at room temperature. The concentration was 4 mM in a 1-mm path-length cell with ca. $250 \mu\text{J}$ /pulse laser power. The solid line is a multi-Gaussian fit of the data. The experimental arrangement is described in ref 8.

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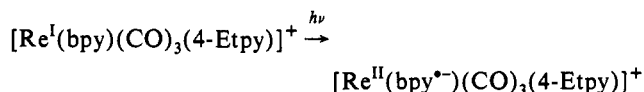
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metal–CO and –CN stretching vibrations have high oscillator strengths, providing high sensitivity. We describe here a novel application of the technique to the elucidation of intramolecular energy transfer in the ligand-bridged complex $[(\text{phen})(\text{CO})_3\text{Re}^{\text{I}}(\text{NC})\text{Ru}^{\text{II}}(\text{CN})(\text{bpy})_2]^+$ (phen is 1,10-phenanthroline; bpy is 2,2'-bipyridine).⁹

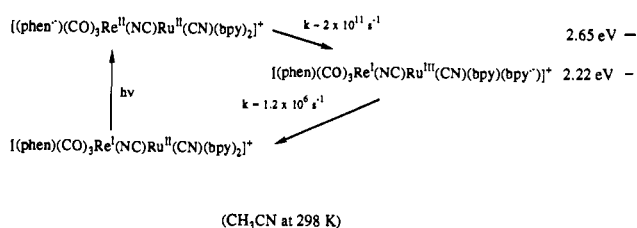
In Figure 1B is shown the transient infrared difference spectrum obtained 200 ns after 354.7-nm excitation of $[(\text{phen})(\text{CO})_3\text{Re}^{\text{I}}(\text{NC})\text{Ru}^{\text{II}}(\text{CN})(\text{bpy})_2]^+$ in CH_3CN . At this wavelength, both $\text{Re}^{\text{I}} \rightarrow \text{phen}$ ($\sim 50\%$) and $\text{Ru}^{\text{II}} \rightarrow \text{bpy}$ ($\sim 50\%$) transitions are excited. From nanosecond transient absorption experiments following laser flash photolysis, an intermediate appears during the laser pulse (~ 7 ns) and decays to the ground state with $\tau = 853$ ns ($k = 1.2 \times 10^6 \text{ s}^{-1}$).⁹ In the ground state, infrared bands are observed at 1920, 2028, 2078, and 2098 cm^{-1} in the region 1800–2200 cm^{-1} . The first two bands are $\nu(\text{CO})$ stretches, and the latter two are the terminal and bridging $\nu(\text{CN})$ stretches.

In Figure 1A is shown the transient spectrum for *fac*- $[\text{Re}^{\text{I}}(\text{bpy})(\text{CO})_3(4\text{-Etpy})]^+$ (4-Etpy is 4-ethylpyridine) in CH_3CN under the same conditions. Here $\text{Re}^{\text{I}} \rightarrow \text{bpy}$ excitation at 354.7 nm gives the metal-to-ligand charge transfer (MLCT) excited state.¹⁰



Infrared bleaches are observed at the ground state $\nu(\text{CO})$ energies 1931 and 2036 cm^{-1} . Excited-state bands appear at 1988, 2015, and 2075 cm^{-1} . The increases ($\Delta\nu(\text{CO}) \sim 57, 84,$

Scheme I



and 39 cm⁻¹) are consistent with oxidation at the metal.¹¹ The splitting of the 1930-cm⁻¹ band into two bands in the excited state is expected upon reduction at bpy. In the ground state, the three N atoms bound to Re (two bpy, one pyridine) are nearly equivalent, giving effective C_{3v} symmetry and two ν(CO) bands. Formation of (bpy⁻) lowers the symmetry to C_s, and three ν(CO) bands are active.¹²

Following 354.7-nm excitation of [(phen)(CO)₃Re^I(NC)Ru^{II}(CN)(bpy)₂]⁺, the shifts in ν(CO) are much smaller (Δν(CO) ~ 5 cm⁻¹), and the terminal ν(CN) shifts from 2078 to 2135 cm⁻¹. (The bridging ν(CN) does not appear in the spectrum; it may overlap the terminal ν(CN) or have a lower oscillator strength.) These observations are consistent with oxidation states Re^I and Ru^{III} in the intermediate formed by laser flash photolysis. They also prove that rapid Re^{II}(phen⁻) → Ru^{II}(bpy) energy transfer occurred following Re^I → phen excitation, Scheme I.

The complex was further interrogated with use of ultrafast infrared measurements.¹³ At the earliest observable times in this experiment (~1 ps, Figure 2A), two transient CO bands appear between 1960 and 2010 cm⁻¹ and a third at 2070 cm⁻¹. These bands decay, and new bands grow at 1936 and 2040 cm⁻¹ with τ ~ 5–10 ps. The 1-ps difference spectrum is very similar to the nanosecond spectrum of fac-[Re^I(bpy)(CO)₃(4-Etpy)]⁺ (Figure 1B), consistent with Re^{II}(phen⁻) at very early times.^{14,15} The CO features which grow and are shown in the spectrum 40 ps after excitation (Figure 2B) are consistent with the appearance of Ru^{III}(bpy⁻) by comparison with the nanosecond results in Figure

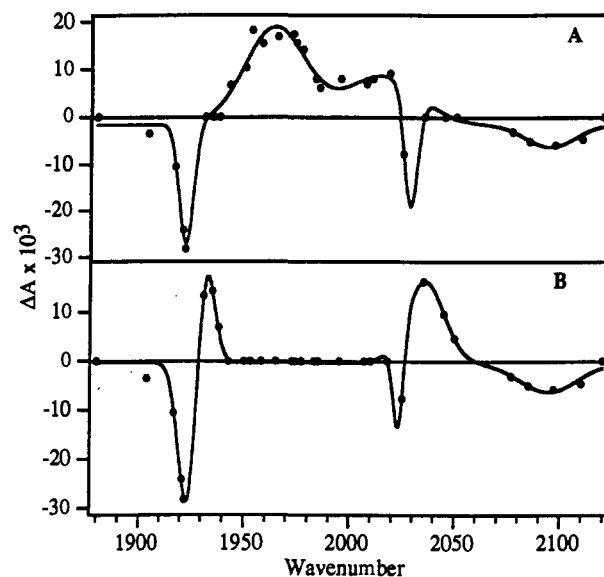


Figure 2. (A) Transient spectrum 1 ps after 300 nm excitation of [(phen)(CO)₃Re^I(NC)Ru^{II}(CN)(bpy)₂]⁺ in acetonitrile at room temperature with instrumentation as described in ref 13. (B) Transient spectrum 40 ps after 300-nm excitation of [(phen)(CO)₃Re^I(NC)Ru^{II}(CN)(bpy)₂]⁺ in acetonitrile at room temperature.

1A. These observations identify the initial MLCT excited state and allow an estimate to be made of the rate constant for energy transfer ($k \sim 2 \times 10^{11} \text{ s}^{-1}$), which is favored by ~0.4 eV.

These results show that the transient infrared technique can be a powerful tool for the elucidation of oxidation state and mechanisms involving photochemical intermediates by direct observation of ligand vibrations.

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(14) In the picosecond infrared experiment, excitation was with 300-nm laser pulses, which leave enough excess energy to pump vibrational excited bands ($v = 1$ and $v = 2$) for the CO stretches. However, with expected vibrational anharmonicities of ca. 15 cm⁻¹ for metal-bound CO's,¹⁵ the band shifts in Figure 2A are too large to result from vibrational relaxation.

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