

# TIME-RESOLVED, STEP-SCAN FTIR STUDIES OF EXCITED STATES OF $d^6$ METAL POLYPYRIDINE COMPLEXES

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Time-resolved infrared spectroscopy using step-scan FTIR has been developed as an approach to study transient inorganic species with lifetimes ranging from ca. 200 nanoseconds to several microseconds. This approach has been applied to a variety of problems arising following laser excitation of  $d^6$  polypyridine complexes in solution, and several examples are shown to demonstrate the utility of this experiment.

*Keywords:* Time-resolved infrared; step-scan infrared; excited state;  $d^6$  metal polypyridine complexes

## INTRODUCTION

Time-resolved infrared spectroscopy compliments the more often used time-resolved resonance Raman approach in the study of excited states of inorganic complexes. With the advances made recently in transient infrared spectroscopy, spectra can now be measured on the time scales previously only obtained by the transient Raman method. The transient infrared technique is particularly valuable in the study of metal complexes containing CO or  $CN^-$  that have intense  $\nu(CO)$  and  $\nu(CN)$  bands [1]. A new and potentially valuable approach to transient infrared studies of excited states on the nanosecond time scale uses step-scan interferometry [2, 3]. Examples demonstrating the utility time-resolved, step-scan FTIR (TRssFTIR) spectroscopy in the study of excited states in  $d^6$  metal polypyridyl complexes are presented.

## EXPERIMENTAL

Experiments were carried out on a modified BioRad FTS 60A/896 step-scan FTIR spectrometer. In the optical arrangement, the IR beam from the interferometer is directed to an external optical train to a lens that focuses the IR radiation onto the sample to a size of less than 3 mm. The transmitted IR beam is collected by a second lens that focuses it onto an element of a photoconductive mercury cadmium telluride (MCT) detector (Graseby 1710117, rise time  $\sim 200$  ns). A low-pass germanium filter coupled with the  $\text{CaF}_2$  cell windows and optics provides a spectral window of 1250 to  $2250\text{ cm}^{-1}$ . The signal is amplified (Graseby DP-8000-4 amplifier) and processed by a BioRad Fast TRS board (200 ns time-resolution) installed in a Pentium PC. The third harmonic (354.7 nm) of a Q-switched Nd:YAG laser was used as the pump source (Spectra Physics DCR-11). The laser timing was controlled by a digital delay generator (Stanford Research Systems Model DG535) which was triggered at the beginning of each interferometer step.

## RESULTS AND DISCUSSIONS

The time-resolved, step-scan FTIR (TRssFTIR) approach has been applied to the study of electronic structure of the excited states of  $\text{Re}(\text{CO})_3$  complexes. A complex interplay between metal-to-ligand charge transfer (MLCT) and ligand-based excited states is known to exist in these complexes and TRssFTIR has been utilized to distinguish between them.

An example of an MLCT excited state is *fac*- $[\text{Re}(\text{phen})(\text{CO})_3(4\text{-Mepy})]^+$  (phen is 1,10-phenanthroline 4-Mepy is 4-methylpyridine) [3]. The TRIR and FTIR spectra for *fac*- $[\text{Re}(\text{phen})(\text{CO})_3(4\text{-Mepy})]^+$  in the  $\nu(\text{CO})$  region are shown in Figure 1. In this spectrum, the broad, ground-state  $\nu(\text{CO})$  band at  $1931\text{ cm}^{-1}$  appears as a bleach with new excited-state bands appearing at 1965 and  $2015\text{ cm}^{-1}$ . The third  $\nu(\text{CO})$  band at  $2036\text{ cm}^{-1}$  also shifts to higher energy ( $2065\text{ cm}^{-1}$ ) in the excited state. The relatively large shifts to higher energy are consistent with partial oxidation of Re(I) to Re(II) and formation of the MLCT state. The shift to higher energy is due to a decrease in Re-CO

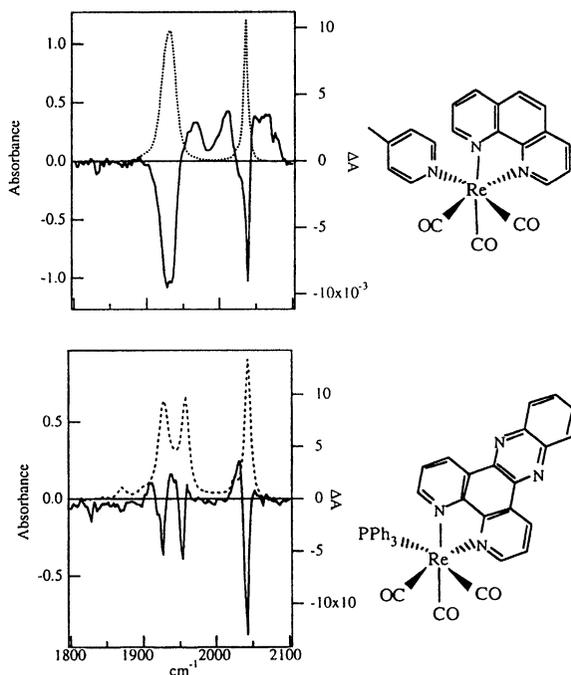


FIGURE 1 FTIR (broken curve) and TRsFTIR spectra of *fac*-[Re(phen)(CO)<sub>3</sub>(4-Mepy)]<sup>+</sup> (top, phen is 1,10-phenanthroline; 4-Mepy is 4-methylpyridine) and *fac*-[Re(dppz)(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup> (bottom, dppz is dipyrido[3,2-a:2',2'-c]phenazine; PPh<sub>3</sub> is triphenylphosphine) at room temperature in CH<sub>3</sub>CN. The transient difference spectra were measured 600 ns after 354.7 nm excitation.

backbonding to Re(II) causing an increase in the triple bond character of the CO ligands.

In contrast, *fac*-[Re(dppz)(CO)<sub>3</sub>(PPh<sub>3</sub>)]<sup>+</sup>\* (dppz is dipyrido [3,2-a:2',2'-c]phenazine; PPh<sub>3</sub> is triphenylphosphine) is classified as having LC lowest excited states (a lowest-lying, dppz-based <sup>3</sup>ππ\* state)[4]. The transient infrared difference spectra for this complex (Fig. 1) shows only slight shifts for the three carbonyl bands to lower energy (< 5 cm<sup>-1</sup>)[3, 5]. The shifts are consistent with a ligand-localized excited state which is slightly more electron donating at the metal relative to the ground state. This monitoring of the carbonyl shifts is very useful in distinguishing excited state character and is

being extended to complicated excited state behavior including dual or mixed excited states and charge-separated states.

A common structural motif in many molecular assemblies based on polypyridyl complexes is ligand bridging. The use of ligand bridges provides a basis for creating complex oligomeric assemblies. Several molecular assemblies which undergo intramolecular energy transfer following excitation have been studied with TRssFTIR spectroscopy. These include cyano-bridged ReRu complexes and polypyridyl-bridged ReRu and ReRe complexes.

$[(\text{phen})(\text{CO})_3\text{Re}(\text{NC})\text{Ru}(\text{bpy})_2(\text{CN})]^+$  is an example of a polynuclear complex designed to produce vectorial energy transport. Energy transfer is expected from the higher energy Re-based MLCT state to the Ru-based MLCT state [6]. The time-resolved resonance Raman and TRssFTIR spectra of this complex following 354.7-nm excitation are shown in Figure 2. In the FTIR spectrum of the ground state,  $\nu(\text{CO})$  bands appear at 1920 and 2028  $\text{cm}^{-1}$ , and  $\nu(\text{CN})$  bands appear for the bridge at 2100  $\text{cm}^{-1}$  and for the terminal cyanide at 2081  $\text{cm}^{-1}$ . The transient Raman spectrum is indicative of bpy radical anion, while the TRssFTIR spectrum shows the terminal  $\nu(\text{CN})$  band shifting from 2081 to 2108  $\text{cm}^{-1}$  with the shifts in the  $\nu(\text{CO})$  bands being small (+5  $\text{cm}^{-1}$ ) compared to the large shifts for  $\text{Re}^{\text{II}}(\text{bpy}^-)$  MLCT states. These observations are consistent with the oxidation states  $\text{Re}^{\text{I}}$  and  $\text{Ru}^{\text{III}}$  in the ns transient intermediate, and the fact that rapid  $\text{Re}^{\text{II}}(\text{phen}^-) \rightarrow \text{Ru}^{\text{II}}(\text{bpy})$  energy transfer occurs following  $\text{Re}^{\text{I}} \rightarrow \text{phen}$  excitation.

The bridging ligand can provide control over intercomponent processes, serving not only as a structural link but also as a means to modulate electron or energy transfer. The complex  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$  (AB is 2,2':3'2'':6'',2''' -quaterpyridine, Fig. 3) is an example where an asymmetric bridge (AB) contains two inequivalent metal binding sites, one more sterically hindered than the other [7]. The difference in the A and B sites is expected to perturb the MLCT energy level of the attached Re(I) or Ru(II) chromophores, thereby controlling the direction of energy transfer in the ReABRu and RuABRe isomers.

The excited state of  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$  in  $\text{CH}_3\text{CN}$  has been characterized by TRssFTIR spectroscopy [3]. The  $\nu(\text{CO})$  bands demonstrate a slight shift to lower energy following excitation. The

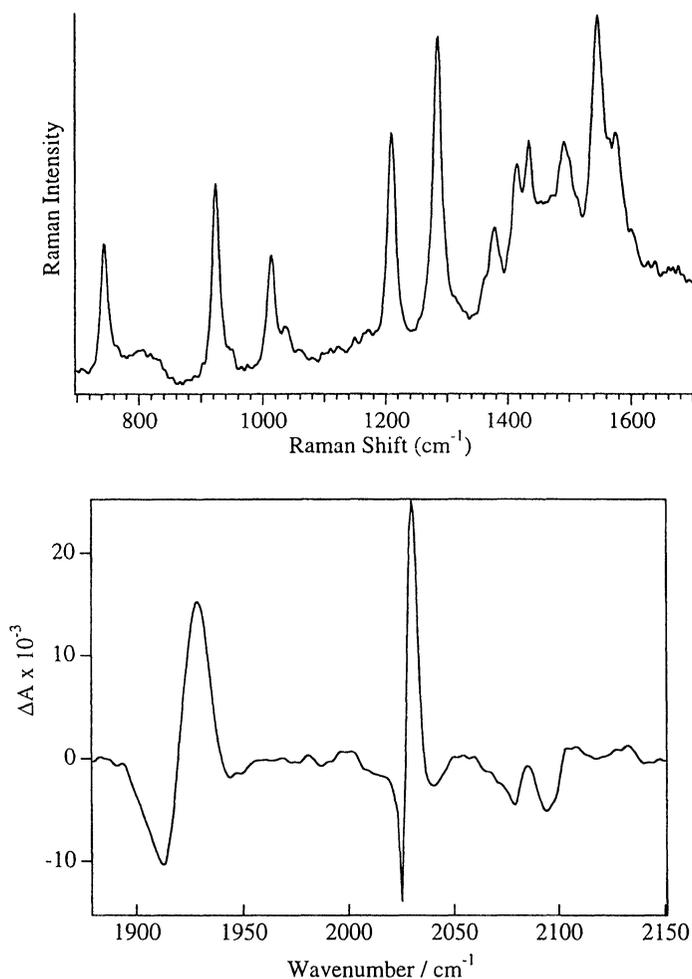


FIGURE 2 Time-resolved resonance Raman spectrum (top, 700–1700 cm<sup>-1</sup>) and TRssFTIR spectrum (bottom, 1850–2150 cm<sup>-1</sup>) of [(phen)(CO)<sub>3</sub>Re(NC)Ru(bpy)<sub>2</sub>(CN)]<sup>+</sup> in CH<sub>3</sub>CN at room temperature.

band at 2023 shifts to 2016 cm<sup>-1</sup>, while the band at 1918 shifts to 1910 cm<sup>-1</sup> and 1902 to 1888 cm<sup>-1</sup>. The magnitude and direction of these shifts suggest that, following initial excitation into MLCT transitions centered on the Re or the Ru, energy transfer occurs to give a Ru<sup>III</sup>-AB<sup>-</sup>MLCT state, [(bpy)<sub>2</sub>Ru<sup>III</sup>(AB<sup>-</sup>)Re<sup>I</sup>(CO)<sub>3</sub>Cl]<sup>2+\*</sup>. The

reduced AB bridge effectively increases the electron density on the Re, causing an increase in  $\pi$  backbonding and a decrease in the  $\nu(\text{CO})$  energy. In contrast for the ReABRu isomer, the TRssFTIR data suggest the presence of both a  $\text{Re}^{\text{II}}\text{-AB}^{\text{-}}$  and a  $\text{Ru}^{\text{III}}(\text{AB}^{\text{-}})$  MLCT excited state at room temperature.

By extending TRssFTIR studies to the fingerprint region, changes in polypyridine IR bands can be monitored. One example is the study of electron localization in the MLCT excited state of tris-homoleptic complexes such as  $[\text{Ru}(\text{bpy})_3]^{2+}$ . In this experiment, all IR-active bands which undergo a change in energy or intensity contribute to the

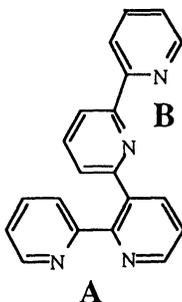


FIGURE 3 Structure of the AB ligand (2,2':3'2'':6'',2'''-quaterpyridine).

TABLE I Infrared band energies from the TRssFTIR spectra of for  $[\text{Ru}(\text{bpy})_3]^{2+*}$  and  $[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-Etpy})]^{+*}$

$[\text{Ru}(\text{bpy})_3]^{2+*}$	$[\text{Re}(\text{bpy})(\text{CO})_3(4\text{-Etpy})]^{+*}$	Origin
1608		$\text{Ru}^{\text{III}}(\text{bpy})$
1548	1547	$\text{bpy}^{\text{-}}$
	1524	$\text{Re}^{\text{II}}(4\text{-Etpy})$
1500	1494	$\text{bpy}^{\text{-}}$
1490		$\text{Ru}^{\text{III}}(\text{bpy})$
	1483	$\text{Re}^{\text{II}}(4\text{-Etpy})$
1469		$\text{Ru}^{\text{III}}(\text{bpy})$
1462	1466	$\text{bpy}^{\text{-}}$
1449	1454	$\text{bpy}^{\text{-}}$
1444		$\text{Ru}^{\text{III}}(\text{bpy})$
1427		$\text{Ru}^{\text{III}}(\text{bpy})$
1420	1425	$\text{bpy}^{\text{-}}$

difference spectrum providing an unambiguous assignment of the excited-state structure.

The first time-resolved infrared difference spectra for MLCT excited states in the fingerprint region (1400–1625 cm<sup>-1</sup>) have been reported for [Ru(bpy)<sub>3</sub>]<sup>2+\*</sup> and [Re(bpy)(CO)<sub>3</sub>(4-Etpy)]<sup>+\*</sup> in CD<sub>3</sub>CN at 298 K [8]. The spectra are assigned by comparison to ground-state spectra and electrochemically generated [Ru<sup>III</sup>(bpy)<sub>3</sub>]<sup>3+</sup> and [Ru<sup>II</sup>(bpy<sup>-</sup>)(bpy)<sub>2</sub>]<sup>+</sup> (Tab. I). The data provide conclusive evidence for the localized description [Ru<sup>III</sup>(bpy<sup>-</sup>)(bpy)<sub>2</sub>]<sup>2+\*</sup> on the ~100 nanosecond time scale.

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