

## Time-Resolved Infrared Studies on Two Isomeric Ruthenium(II)/Rhenium(I) Complexes Containing a Nonsymmetric Quaterpyridine Bridging Ligand

Jon R. Schoonover,\* Andrew P. Shreve, and R. Brian Dyer

Chemical Science and Technology Division,  
Mail Stop J586, Los Alamos National Laboratory,  
Los Alamos, New Mexico 87545

Rosemary L. Cleary and Michael D. Ward

School of Chemistry, University of Bristol,  
Cantock's Close, Bristol, U.K.

Carlo A. Bignozzi

Dipartimento di Chimica, Università di Ferrara, Ferrara, Italy

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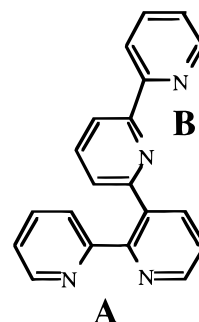
### Introduction

The control of light-induced intramolecular energy and electron transfer in inorganic complexes is an area of current work, and considerable success in this field has been achieved by tuning chemical structure.<sup>1,2</sup> Such success requires a substantial understanding of the electronic and nuclear properties of excited states. Complexes consisting of two or more transition metal complex subunits linked by a bridging ligand are of particular interest.<sup>2</sup> In such systems, the nature of the bridging ligand helps control energy and electron transfer between the metal centers. The study of excited-state processes in these complexes by optical absorption and emission spectroscopies is often complicated by overlapping contributions from the multiple metal centers. In many such cases, time-resolved vibrational spectroscopy can be used to obtain specific information about the nature of excited states.<sup>3</sup>

\* To whom correspondence should be addressed. Fax: 505-667-0851. E-mail: schoons@lanl.gov.

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In this paper, time-resolved infrared (TRIR) spectroscopy is used to study the lowest energy metal-to-ligand charge transfer (MLCT) excited state of the isomeric complexes [(bpy)<sub>2</sub>Ru<sup>II</sup>-ABRe(CO)<sub>3</sub>Cl]<sup>2+</sup> (RuABRe) and [(CO)<sub>3</sub>ClRe<sup>I</sup>ABRu<sup>II</sup>(bpy)<sub>2</sub>]<sup>2+</sup> (ReABRu; AB is 2,2':3',2'':6'',2'''-quaterpyridine; bpy is 2,2'-bipyridine).<sup>4</sup> The AB bridge is asymmetric and contains two electronically inequivalent metal-binding sites due to different bipyridyl substitution patterns, and the B site is more sterically hindered. The difference in these binding sites is expected to perturb the energies of the MLCT states for attached Re(I) or Ru(II) subunits. In fact, an earlier study demonstrated that at room temperature the visible luminescence is Ru-based for the RuABRe isomer and Re-based for the ReABRu isomer, suggesting that the lowest energy state and the direction of energy transfer in these isomers are actually reversed.<sup>4</sup> However, this result was based on luminescence lifetimes and could be influenced by the establishment of an equilibrium between an intrinsically longer lived Ru-based excited state and a shorter lived Re-based excited state, leaving open the possibility that the Ru-based MLCT is lower in energy in both cases. Time-resolved vibrational spectroscopy is useful to resolve this ambiguity since the ν(CO) bands for the carbonyl ligands on Re are an excellent probe of the excited-state electronic distribution in these complexes. Infrared difference spectra have been measured following photoexcitation and the data analyzed to address the orbital origin of the excited state, the transient oxidation states of the metals, and specifically, the possibility of the presence of equilibrated states having different electronic configurations.



### Experimental Section

**Nanosecond Experiments.** Nanosecond TRIR spectra were measured using a previously described step-scan FTIR approach.<sup>5</sup> Samples were dissolved in CH<sub>3</sub>CN to a concentration that yielded a ground-state IR absorption of between 0.7 and 1.1 (in a 1 mm path length

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cell) for the most intense  $\nu(\text{CO})$  band. In this experiment the transient signal was integrated for 400 ns following excitation at 354.7 nm with a 10 ns pulse. The difference spectrum is the average of 16 co-added scans.

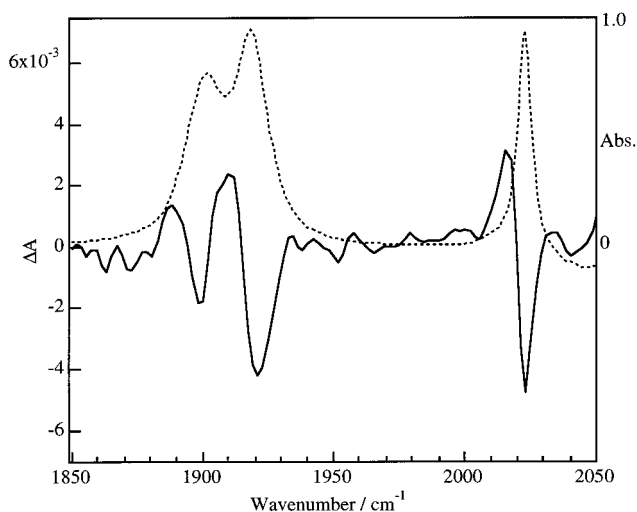
**Picosecond Experiments.** Picosecond TRIR spectra were measured on a system to be described fully elsewhere.<sup>6</sup> Briefly, the laser is based on a Ti:sapphire regenerative amplifier that operates with a 1 kHz repetition rate, producing 180 fs pulses of  $\approx 600 \mu\text{J}$  centered at 810 nm. The 810 nm pulse is split into two arms, with one arm being doubled to create an excitation pulse centered at 405 nm. The other arm is used to pump an optical parametric generator and amplifier to generate pulses of up to  $30 \mu\text{J}$  at tunable signal and idler wavelengths. The signal and idler outputs are then recombined in a  $\text{AgGaS}_2$  crystal to generate mid-infrared light at their difference frequency. Typical operation yields greater than  $1 \mu\text{J}$  of infrared light having an energy spectrum with breadth of approximately  $150 \text{ cm}^{-1}$  (fwhm). The infrared light is split to form independent probe and reference beams by reflection off an uncoated Si wafer. The probe beam is overlapped spatially with the 405 nm pump beam in the sample, while the reference beam passes through an unexcited region of the sample. Following the sample, the probe and reference beams are directed through an infrared monochromator and gently focused onto matched MCT detectors. The outputs of the MCT detectors are sampled, and the ratio of the outputs serves as an input signal for a lock-in detector that is synchronized to an optical chopper modulating the pump beam. For a fixed time delay between the pump and probe pulses, generated by an optical delay line, pump-on minus pump-off difference spectra are obtained by monitoring the output of the lock-in detector while scanning the infrared monochromator. This signal is normalized by the ratio of the probe and reference signals to yield  $\Delta T/T$ , which is then converted to  $\Delta A$  for presentation.

For the picosecond experiments, samples were dissolved in  $\text{CH}_3\text{CN}$  to a concentration adjusted to yield an optical density of  $\approx 0.8$  at 405 nm for a 1 mm path length. At this concentration, the  $\nu(\text{CO})$  band at  $2023 \text{ cm}^{-1}$  had an absorptivity of  $\approx 0.3$  in a 1 mm path length. The magnitude of features in the difference spectra varied linearly with excitation intensity for pump pulse energies ranging from 3 times less to 1.5 times greater than the  $2 \mu\text{J}$  (focused to an  $\approx 250 \mu\text{m}$  diameter spot size) normally used.

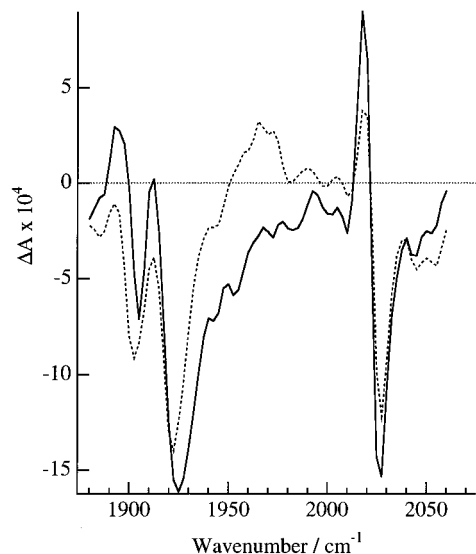
## Results

The isomer  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$ , which has a relatively long-lived excited state ( $\tau = 410 \text{ ns}$ ), was studied using nanosecond TRIR. The step-scan FTIR difference spectrum, along with the ground-state FTIR spectrum, is shown in Figure 1. The ground-state spectrum exhibits bands at 1902, 1918, and  $2023 \text{ cm}^{-1}$ . In the transient difference spectrum bleaches appear at 1899, 1921, and  $2023 \text{ cm}^{-1}$ , while positive signals are observed at 1888, 1910, and  $2016 \text{ cm}^{-1}$ . Collectively, these features in the difference spectrum indicate that each of the  $\nu(\text{CO})$  bands is shifted slightly to lower energy.

Because of the shorter excited-state lifetime of  $[(\text{CO})_3\text{Cl-Re}^{\text{I}}\text{ABRu}^{\text{II}}(\text{bpy})_2]^{2+}$  ( $\tau = 23 \text{ ns}$ ), the nanosecond TRIR experiment cannot measure the difference spectrum associated with the excited state of this species with reasonable signal-to-noise. An ultrafast TRIR approach is required, and the identical ultrafast experiment was also performed on the  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$  complex. The difference spectra, representing the excited-state absorption minus the ground-state absorption 100 ps after excitation with 405 nm pulses, are presented in Figure 2. For  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$ , the difference spectrum 100 ps following excitation is essentially identical to the difference spectrum obtained for this complex on the nanosecond time scale (Figure 1). Bleaches are observed at 1905, 1925, and  $2028 \text{ cm}^{-1}$ , with positive signals at 1895, 1912, and  $2018 \text{ cm}^{-1}$ , again suggesting a slight shift of each of the



**Figure 1.** FTIR spectrum (broken line) and time-resolved, step-scan FTIR difference spectrum (solid line) of  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$  (AB is 2,2':3',2'':6'',2'''-quaterpyridine) in  $\text{CH}_3\text{CN}$  at room temperature. The transient spectrum was measured during 400 ns after 354.7 nm (100–200  $\mu\text{J}/\text{pulse}$ , 10 ns) excitation with  $4 \text{ cm}^{-1}$  resolution and is the average of 16 co-added scans. The sample concentration was ca. 1 mM contained in a 1 mm path length cell.

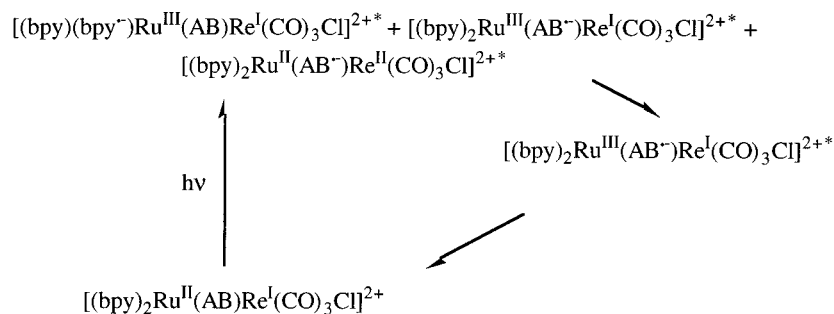
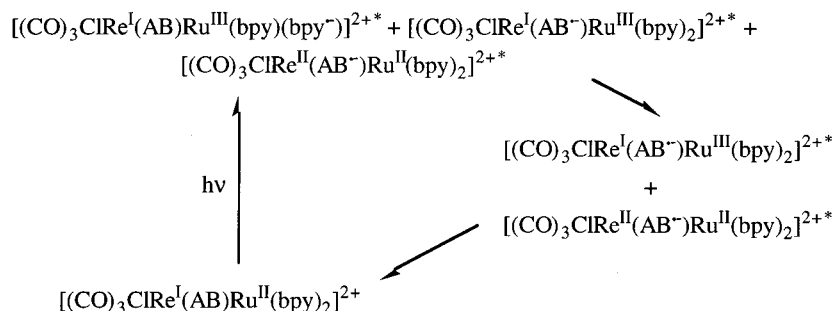


**Figure 2.** Infrared difference spectra of  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$  (solid line) and  $[(\text{CO})_3\text{ClRe}^{\text{I}}\text{ABRu}^{\text{II}}(\text{bpy})_2]^{2+}$  (broken line) 100 ps after 405 nm excitation in  $\text{CH}_3\text{CN}$  at 298 K. The experimental setup and conditions are described in the Experimental Section.

$\nu(\text{CO})$  bands to lower energy in the excited state. In contrast, the difference spectrum 100 ps following excitation for the  $[(\text{CO})_3\text{ClRe}^{\text{I}}\text{ABRu}^{\text{II}}(\text{bpy})_2]^{2+}$  isomer has similar, but weaker, positive features at 1892, 1912, and  $2018 \text{ cm}^{-1}$  along with bleaches at 1902, 1922, and  $2028 \text{ cm}^{-1}$ . This spectrum also has a new, broad, positive feature near  $1965 \text{ cm}^{-1}$ .

## Discussion

Laser pulses at either 354.7 or 405 nm simultaneously excite metal-to-ligand charge transfer (MLCT) transitions centered on both ends of the two isomers. Subsequent steps involving either energy or electron transfer lead to the lowest energy excited state, and two observations indicate that this evolution is complete within 100 ps. First, although spectral evolution is observed at very early times (much less than 100 ps) following excitation,<sup>7</sup> the transient difference spectra of both complexes

Scheme 1<sup>a</sup><sup>a</sup> CH<sub>3</sub>CN, 298 K.Scheme 2<sup>a</sup><sup>a</sup> CH<sub>3</sub>CN, 298 K.

are fully evolved and stable within 100 ps. Second, as evident from the data shown in Figures 1 and 2, for the longer lived excited state,  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+*}$ , the spectra measured at 100 ps and on the nanosecond time scale are nearly identical. Thus, the discussion will center on comparison and interpretation of the spectra obtained for the two complexes at 100 ps following excitation with the assumption that these spectra interrogate the relaxed excited state in both complexes.

For  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+*}$ , the difference spectra measured 100 ps after excitation and on the nanosecond time scale both indicate slight shifts of the  $\nu(\text{CO})$  bands to lower energy compared to the ground state. This result is consistent with an increase of electron density on the Re, leading to an increase in  $\pi$  back-bonding and a slight decrease in the energies of the three  $\nu(\text{CO})$  bands. Population of an antibonding orbital in the AB bridge could lead to this result, and shifts in this direction have been observed in ligand-centered excited states in  $\text{Re}^{\text{I}}(\text{CO})_3(\text{polypyridine})$  monomers.<sup>5,8</sup> In the present case, the increase in electron density on the Re leads us to assign the excited state as being a  $\text{Ru}^{\text{II}} \rightarrow \text{AB}$  MLCT state, best described as  $[(\text{bpy})_2\text{Ru}^{\text{III}}(\text{AB}^-)\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+*}$ , an interpretation consistent with the assignment of Ru-based luminescence for this complex.<sup>4</sup> Thus, for  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$ , simultaneous  $\text{Re} \rightarrow \text{AB}$ ,  $\text{Ru} \rightarrow \text{AB}$ , and  $\text{Ru} \rightarrow \text{bpy}$  MLCT excitation results in a relaxed excited state best described as  $[(\text{bpy})_2\text{Ru}^{\text{III}}(\text{AB}^-)\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+*}$  which forms in less than 100 ps (Scheme 1).

The transient spectrum of  $[(\text{CO})_3\text{ClRe}^{\text{I}}\text{ABRu}^{\text{II}}(\text{bpy})_2]^{2+*}$  also exhibits features indicative of slight shifts of the  $\nu(\text{CO})$  bands

to lower energy, but these features appear with reduced intensity. This suggests the presence of some excited-state population that can be described as  $[(\text{CO})_3\text{ClRe}^{\text{I}}(\text{AB}^-)\text{Ru}^{\text{III}}(\text{bpy})_2]^{2+}$ . In contrast to the difference spectrum of the RuABRe isomer, this spectrum demonstrates a much narrower bleach near  $1925\text{ cm}^{-1}$  and a broad positive absorption near  $1965\text{ cm}^{-1}$ . This absorption is consistent with an approximately  $60\text{ cm}^{-1}$  shift to higher energy of the ground-state  $\nu(\text{CO})$  bands at  $1902$  and  $1918\text{ cm}^{-1}$ . This feature is similar to that observed for the 1 ps TRIR spectrum of the  $\text{Re}^{\text{II}}(\text{phen}^-)$  state for  $[(\text{phen})(\text{CO})_3\text{Re}(\text{NC})\text{Ru}(\text{bpy})_2(\text{CN})]^{+}$ .<sup>9</sup> Such large shifts to higher energy are also similar to those observed for MLCT excited states of  $\text{Re}(\text{I})$  monomers such as  $[(1,10\text{-phenanthroline})\text{Re}^{\text{I}}(\text{CO})_3(4\text{-methylpyridine})]^{+}$  and  $[(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3(4\text{-ethylpyridine})]^{+}$ .<sup>5,8</sup> For this reason, this feature is assigned to originate from the presence of some excited-state population best described as  $[(\text{CO})_3\text{ClRe}^{\text{II}}(\text{AB}^-)\text{Ru}^{\text{II}}(\text{bpy})_2]^{2+}$ . The presence of this excited state should also lead to a shift to higher energy for the  $2025\text{ cm}^{-1}$   $\nu(\text{CO})$  band, but such a shift is too large to be observed due to interference from a solvent absorption band at energies greater than  $2060\text{ cm}^{-1}$ . The large shifts in the  $\nu(\text{CO})$  bands result from partial oxidation of  $\text{Re}(\text{I})$  to  $\text{Re}(\text{II})$ , with a corresponding decrease in  $\text{Re}-\text{CO}$  back-bonding and an increase in the triple-bond character of the CO ligands.

Thus, the transient IR data for  $[(\text{CO})_3\text{ClRe}^{\text{I}}\text{ABRu}^{\text{II}}(\text{bpy})_2]^{2+*}$  indicate the presence of both  $[(\text{CO})_3\text{ClRe}^{\text{I}}(\text{AB}^-)\text{Ru}^{\text{III}}(\text{bpy})_2]^{2+}$  and  $[(\text{CO})_3\text{ClRe}^{\text{II}}(\text{AB}^-)\text{Ru}^{\text{II}}(\text{bpy})_2]^{2+}$  100 ps after 405 nm excitation. At room temperature, the reported luminescence lifetime of this complex suggested emission from a Re-based MLCT state.<sup>4</sup> However, if both excited states exist in thermal equilibrium, the emission lifetime will be largely governed by the intrinsically faster nonradiative decay of the  $\text{Re}^{\text{II}}-\text{AB}^-$

(7) At very early times following photoexcitation, the transient difference spectra contain a broad featureless absorption within which the sharper negative features due to ground-state depletion are evident. This broad absorption has not been definitively assigned, but its evolution, which could be associated with vibrational or electronic relaxation, leads to the fully evolved and stable difference spectra reported here within tens of picoseconds.

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MLCT state. Thus, the IR data are consistent with the luminescence studies of  $[(\text{CO})_3\text{ClRe}^{\text{I}}\text{ABRu}^{\text{II}}(\text{bpy})_2]^{2+}$ , but provide additional evidence to indicate the presence of an equilibration of  $\text{Re}^{\text{II}}-\text{AB}^{\bullet-}$  and  $\text{AB}^{\bullet-}-\text{Ru}^{\text{III}}$  excited states, as shown in Scheme 2. Because the AB bridge is reduced in both states, the transition between the two excited states can be considered to be either an energy transfer between MLCT states or an electron transfer between the two metal centers. The presence of the equilibrated excited states in this complex, but not in the  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{ABRe}^{\text{I}}(\text{CO})_3\text{Cl}]^{2+}$  complex, is consistent with the proposed significant difference in excited-state energies associated with the A and B binding sites of the asymmetric bridging complex.<sup>4</sup>

In conclusion, the current study illustrates the value of time-resolved infrared spectroscopy for probing the nature of excited states in complicated transition metal complexes having multiple metal centers. Often, only a structurally informative probe like vibrational spectroscopy is able to distinguish between the various possibilities that exist for excited-state structure in such complexes. For example, in the present case, while the luminescence lifetimes of MLCT states of the two metal centers

differ significantly, the shapes of their room-temperature emission spectra are similar.<sup>4</sup> Thus, the presence of significant amounts of both excited states in an equilibrium mixture is difficult to determine from luminescence experiments. However, time-resolved infrared spectroscopy clearly demonstrates the presence of such a room-temperature equilibration between two excited states in one of the isomeric complexes studied and has thereby provided unambiguous information about differences in the excited-state structure and energetics of the two complexes.

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