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TITLE: PICOSECOND INFRARED STUDY OF INTRAMOLECULAR ENERGY TRANSFER IN $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^{+}$

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Abstract.

The dynamics and mechanism of intramolecular energy transfer in $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^{+}$ following metal-to-ligand charge transfer excitation have been studied using picosecond infrared spectroscopy.

Picosecond Infrared Study of Intramolecular Energy Transfer in $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^+$

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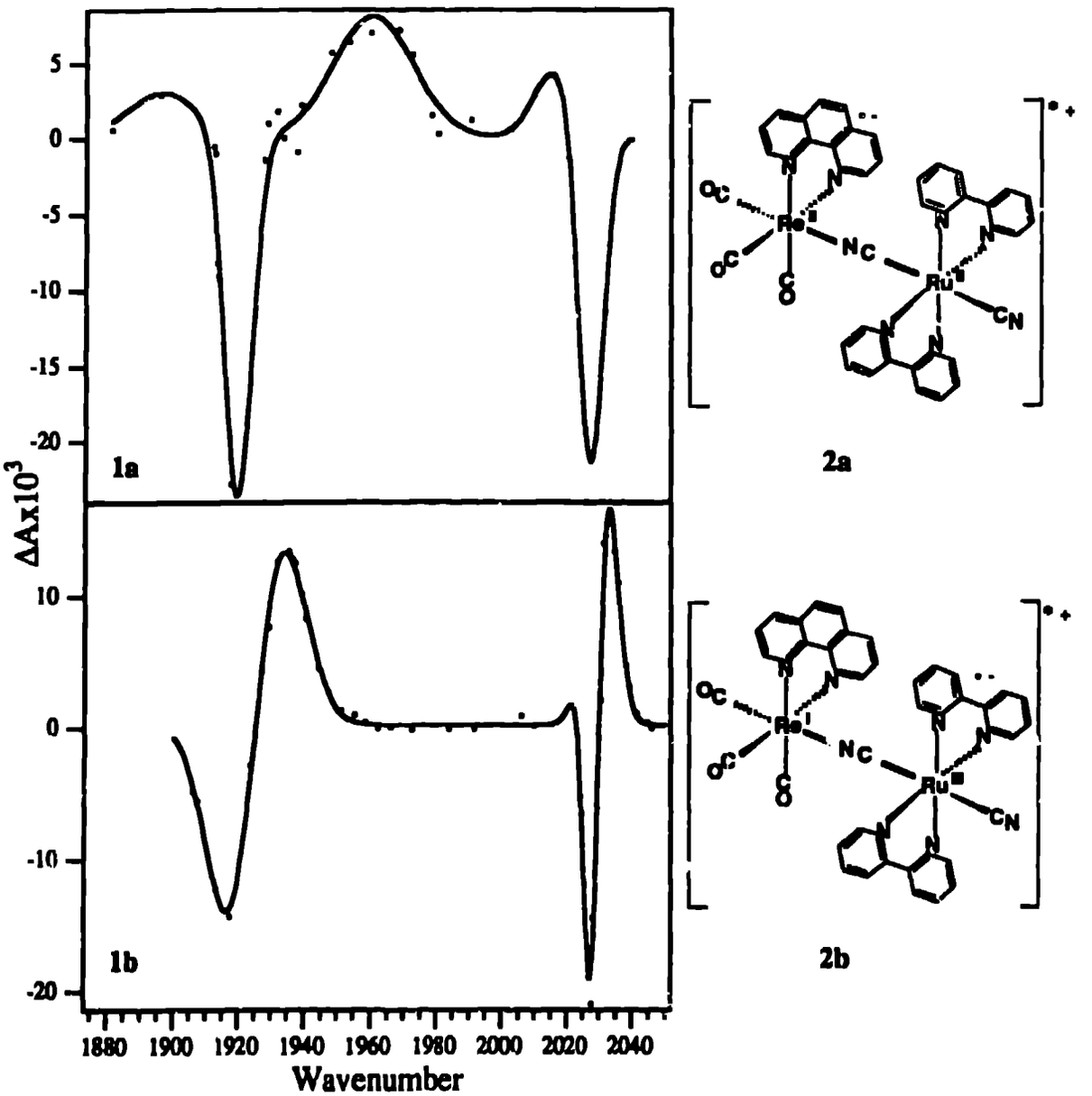
Significant advances have been made in the design and characterization of molecular assemblies which, upon photoexcitation, undergo intramolecular electron or energy transfer.[1] These reactions have typically been followed by transient electronic absorption spectroscopy. This technique, however, suffers from the disadvantage that absorption bands tend to be broad and featureless which can lead to ambiguous interpretation in complex assemblies, especially where there is more than one absorbing chromophore. Time-resolved resonance Raman spectroscopy has been applied to the study of excited states,[2] but time-resolved infrared spectroscopy (TRIR) is particularly well-suited to probing complexes containing ligands such as CO or CN which are bound to the metal.[3] Unlike the transient Raman experiment, TRIR does not rely on resonance enhancement in the excited state since the metal-CO and -CN stretching vibrations have large oscillator strength providing high sensitivity. We describe here a novel application of TRIR spectroscopy to the elucidation of intramolecular energy transfer in the ligand-bridged complex, $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^+$ (phen is 1,10-phenanthroline, bpy is 2,2'-bipyridine),[4] representing the first application of the technique to a process of this type.

Figure 1 shows the TRIR difference spectra in the ν_{CO} stretching region obtained 2 ps (spectrum 1a) after 300 nm excitation and 200 ns (spectrum 1b) after 355 nm excitation of $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(CN)(bpy)_2]^+$ in CH_3CN. Typical of these types of complexes, the broad electronic absorptions of both metal centers overlap considerably such that at these pump wavelengths the excitation of both $Re^{I} \rightarrow$ phen and $Ru^{II} \rightarrow$ bpy metal-to-ligand charge transfer (MLCT) transitions occur. The IR frequencies of the CO and CN bands are very sensitive to metal oxidation state however, making it possible to determine unambiguously the nature of the intermediates formed by the excitation pulse. Assignments are based on comparison to ground and excited state IR spectra of monomeric model complexes.

The 2 ps spectrum indicates that the predominant species present at very early times is the $Re^{I} \rightarrow$ phen MLCT state as illustrated in Fig. 2a. While only two CO bands (1921 and 2028 cm^{-1}) are observed in the ground state, (suggesting effective C_{3v} symmetry for the 3 CO and 3 N ligands), the lowest energy CO band is split (1960 and 1981 cm^{-1}) in the 2 ps spectrum. This splitting is most likely due to symmetry lowering caused by the presence of a hole in the d(π) orbitals of the $Re^{II}(phen^{\cdot-})$ MLCT state. Subsequently this state rapidly (~5 ps) decays to a state which lives for hundreds of nanoseconds and gives the TRIR spectrum shown in Fig. 1b. The small shifts of the CO bands and the large shifts of the CN bands (not shown) are consistent with the assignment of this spectrum to the $Ru^{II} \rightarrow$ bpy MLCT state (Fig. 2b).

The net reaction following $Re^{I} \rightarrow$ phen excitation is $Re^{II}(phen^{\cdot-}) \rightarrow Ru^{III}(bpy^{\cdot-})$ energy transfer which is spontaneous by ~ 0.2 eV and the long-lived intermediate is a mixed-oxidation state complex. The same intermediate is reached by direct $Ru^{II} \rightarrow$ bpy excitation. The dynamics and mechanism of energy transfer will be discussed.



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