

Notes

Time-Resolved IR Studies of $[\text{Re}(\text{LL})(\text{CO})_4]^+$

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Introduction

There is continuing interest in the excited-state behavior of transition metal–carbonyl complexes containing polypyridyl ligands.^{1–4} Their unique photophysical and photochemical properties are useful in a variety of areas, from biochemistry to materials science.^{5–15}

Complexes of the form $[\text{M}(\text{bpy})(\text{CO})_4]$ (M is Cr, Mo, or W, and bpy is 2,2'-bipyridine) exhibit particularly intriguing excited-state behavior. For these complexes, the lowest-lying excited state is typically a metal-to-ligand charge-transfer (MLCT) state, with a close-lying ligand field (LF) state to higher energy.^{16,17} There has been considerable interest in understanding the interplay of these two states. Following initial studies by Wrighton and Morse,^{15,18} Manuta and Lees¹⁹ performed exten-

sive studies on the photosubstitution reactions of $[\text{M}(\text{bpy})(\text{CO})_4]$. Irradiation into either the LF or MLCT absorption band led to substitution, but the quantum yield for photosubstitution decreased considerably for the latter. Manuta and Lees concluded that either the MLCT state is very weakly photoactive, or a low-lying ³LF state (close in energy to the MLCT state and in thermal equilibrium with it) is responsible for the longer-wavelength photochemistry.

Rillema and co-workers observed that the excited-state properties of $[\text{Re}(\text{bpy})(\text{CO})_4]^+$ required the inclusion of a low-lying ligand-centered (LC) state to account for the observed optical properties.^{20,21} High-resolution absorption and luminescence measurements by Strouse and co-workers on a series of single crystals of $[\text{Re}(\text{LL})(\text{CO})_4](\text{PF}_6)$ (LL is 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, or 1,10-phenanthroline) at 298 and 15 K indicated the presence of metal–ligand vibrational sidebands and a shortened luminescence decay, consistent with a ³LC state weakly mixed with the lowest-lying ¹MLCT state.^{22,23} The best description proposed for the excited state in these materials was a nominally LC state with an admixture of 1–3% charge-transfer character arising from a dipole exchange mechanism for wave function mixing.^{22,23}

Time-resolved infrared (TRIR) spectroscopy has proved useful in describing the nature of convoluted excited states of carbonyl-containing complexes in solution.^{24–26} The $\nu(\text{CO})$ bands are particularly helpful due to their high oscillator strengths and interaction with the metal center. In this paper, ground-state and TRIR data are presented in the $\nu(\text{CO})$ region for $[\text{Re}(\text{LL})(\text{CO})_4]^{+*}$ (LL is 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmb), or 1,10-phenanthroline (phen)) in 1,2-dichloroethane following 354.7 nm excitation. Changes in the $\nu(\text{CO})$ bands are used to characterize the photochemical behavior of these complexes. The data demonstrate formation of a unique excited state described by an admixture of CT character into an LC excited state, followed by photolysis of a single carbonyl ligand to form a *fac*- $\text{Re}(\text{CO})_3$ solvento complex.

Experimental Section

Materials. 1,2-Dichloroethane (DCE) was obtained from Aldrich and used without further purification. $[\text{Re}(\text{LL})(\text{CO})_4](\text{PF}_6)$ samples were prepared by literature methods.^{22,23}

Infrared Measurements. A 100 mg sample of $[\text{Re}(\text{LL})(\text{CO})_4](\text{PF}_6)$ was dissolved in 50 mL of DCE and sparged with argon for 15 min. The solution was transferred to a gastight syringe under an inert atmosphere and flowed continuously at 0.34 mL/min through a 0.5 mm fixed-path length CaF_2 IR cell under a positive pressure of argon.

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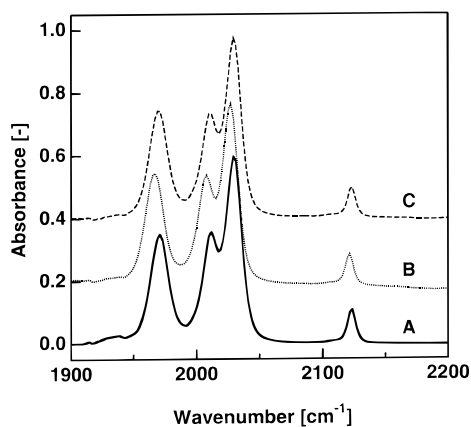


Figure 1. Ground-state IR spectra of $[\text{Re}(\text{phen})(\text{CO})_4]^+$ (A), $[\text{Re}(\text{dmb})(\text{CO})_4]^+$ (B), and $[\text{Re}(\text{bpy})(\text{CO})_4]^+$ (C) in the $\nu(\text{CO})$ region in DCE at 298 K.

Table 1. Ground-State (GS) and Excited-state (ES) $\nu(\text{CO})$ Band Energies in (cm^{-1}) for $[\text{Re}(\text{LL})(\text{CO})_4]^+$ in DCE at 298 K

	$[\text{Re}(\text{bpy})(\text{CO})_4]^+$		$[\text{Re}(\text{dmb})(\text{CO})_4]^+$		$[\text{Re}(\text{phen})(\text{CO})_4]^+$	
	GS	ES	GS	ES	GS	ES
B_2	1969	1973	1967	1971	1971	1975
$2A_1$	2011	2014	2008	2012	2012	2016
B_1	2029	2033	2027	2032	2039	2044
$1A_1$	2123	2118	2122	2112	2123	2118

The optical arrangement of the time-resolved, step-scan FTIR experiment, using a BioRad FTS 60A/896 step-scan FTIR, has been previously described.^{27,28} Data were collected both as spectra at a particular time slice and as time traces at a specific wavenumber. Spectra and traces shown are an average of six scans.

Results

The ground-state IR spectra of the $[\text{Re}(\text{LL})(\text{CO})_4]^+$ complexes in the $\nu(\text{CO})$ region in DCE at 298 K are shown in Figure 1. Each spectrum exhibits four bands, assigned as the $2A_1$, B_1 , and B_2 modes in C_{2v} symmetry. The nature of the polypyridyl ligand has only minor effects on their position and intensity, with a slight shift to lower frequency in the $[\text{Re}(\text{dmb})(\text{CO})_4]^+$ complex arising from increased electron donation to the pyridyl ring. The band energies for the three complexes are listed in Table 1.

Ground- and excited-state infrared difference spectra of $[\text{Re}(\text{phen})(\text{CO})_4]^+$ in the $\nu(\text{CO})$ region are shown in Figure 2, along with the calculated excited-state spectrum (excited-state spectrum = transient difference spectrum + weighted ground-state spectrum). Band energies are listed in Table 1. The three lower-energy ground-state bands shift to higher energy in the excited state by 3–4 cm^{-1} ; the highest-energy ground-state band shifts 5 cm^{-1} to lower energy.

Ground- and excited-state data for $[\text{Re}(\text{dmb})(\text{CO})_4]^+$ in the $\nu(\text{CO})$ region are given in Figure 3 and Table 1. The three lower-energy ground-state bands shift to higher energy in the excited state by 4–5 cm^{-1} ; the highest-energy ground-state band shifts 10 cm^{-1} to lower energy.

Ground- and excited-state data for $[\text{Re}(\text{bpy})(\text{CO})_4]^+$ in the $\nu(\text{CO})$ region are given in Figure 4 and Table 1. The three lower-energy ground-state bands shift to higher energy in the excited

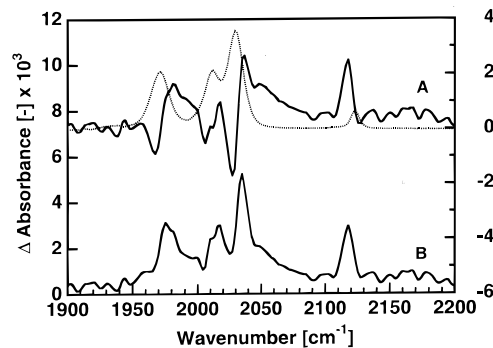


Figure 2. TRIR difference spectra of $[\text{Re}(\text{phen})(\text{CO})_4]^+$ (A, solid line) in the $\nu(\text{CO})$ region in DCE at 298 K. The ground-state spectrum is shown for comparison (A, dotted line). The calculated excited-state spectrum is shown as (B).

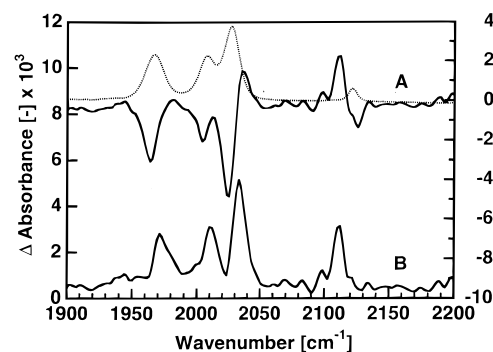


Figure 3. TRIR difference spectra of $[\text{Re}(\text{dmb})(\text{CO})_4]^+$ (A, solid line) in the $\nu(\text{CO})$ region in DCE at 298 K. The ground-state spectrum is shown for comparison (A, dotted line). The calculated excited-state spectrum is shown as (B).

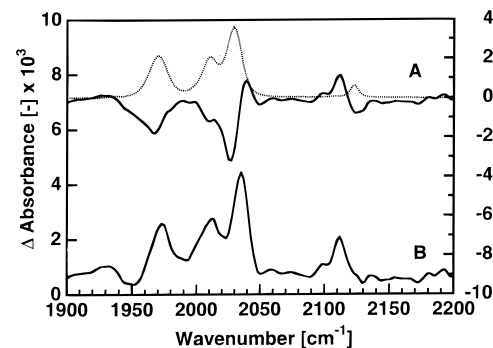


Figure 4. TRIR difference spectra of $[\text{Re}(\text{bpy})(\text{CO})_4]^+$ (A, solid line) in the $\nu(\text{CO})$ region in DCE at 298 K. The ground-state spectrum is shown for comparison (A, dotted line). The calculated excited-state spectrum is shown as (B).

state by 4–5 cm^{-1} ; the highest-energy ground-state band shifts 5 cm^{-1} to lower energy.

Figure 5 shows the decay of the excited-state species (monitored at 2049 cm^{-1}) and the growth of the photolyzed complex (monitored at 2118 cm^{-1}) for $[\text{Re}(\text{phen})(\text{CO})_4]^+$. Thermal effects cause some increased absorbance values in these traces. All three complexes behave in a similar manner following 354.7 nm excitation.

The formations of the photoproduct following the initial excited state are also similar for all three complexes. A broad absorption appears near 1950 cm^{-1} with a narrower band at 2050 cm^{-1} . Band energies are listed in Table 2, and a representative of the spectrum of the photoproduct for $[\text{Re}(\text{phen})(\text{CO})_4]^+$ is shown in Figure 6.

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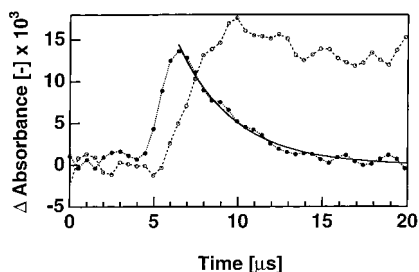


Figure 5. Decay of the excited-state species (···, monitored at 2049 cm^{-1}) and growth of the photolyzed complex (---, monitored at 2118 cm^{-1}) for $[\text{Re}(\text{phen})(\text{CO})_4]^+$ in DCE at 298 K following 354.7 nm excitation.

Table 2. $\nu(\text{CO})$ Band Energies (cm^{-1}) for the Photoproduct of $[\text{Re}(\text{LL})(\text{CO})_4]^+$ Following 354.7 nm Excitation in DCE at 298 K

$[\text{Re}(\text{bpy})(\text{CO})_4]^+$	$[\text{Re}(\text{dmb})(\text{CO})_4]^+$	$[\text{Re}(\text{phen})(\text{CO})_4]^+$
1950	1948	1953
2048	2045	2049

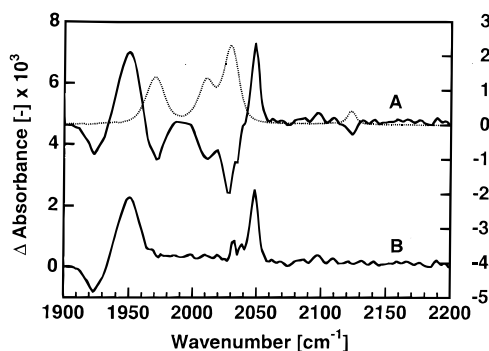
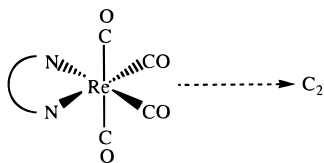


Figure 6. IR spectrum of the photoproduct of $[\text{Re}(\text{phen})(\text{CO})_4]^+$ in the $\nu(\text{CO})$ region in DCE at 298 K following 354.7 nm excitation.

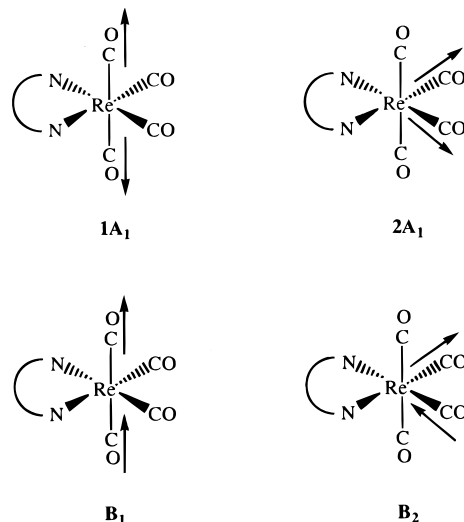
Discussion

Symmetry Considerations. All three $[\text{Re}(\text{LL})(\text{CO})_4]^+$ complexes possess C_{2v} symmetry in the ground and MLCT or LC excited states. The four $\nu(\text{CO})$ bands observed in each spectrum arise from the $2A_1$, B_1 , and B_2 modes in C_{2v} symmetry. With the C_2 axis defined as intersecting the Re center in the plane of the polypyridyl ligand



the four IR-active carbonyl modes can be best described as (1) an A_1 mode involving in-phase motion of the two carbonyls *cis* to the polypyridine ligand, (2) the analogous A_1 mode involving the *trans*-carbonyls, (3) a B_1 mode involving the out-of-phase motion of the *cis*-carbonyls, and (4) the analogous B_2 mode involving the *trans*-carbonyls.

For $[\text{Re}(\text{bpy})(\text{CO})_4]^+$, bands are observed in the ground state at 1969, 2011, 2029, and 2123 cm^{-1} . Using the descriptions of the modes and the normal coordinate analysis of $\text{Cr}(\text{CO})_4(\text{bpy})$,^{29,30} the following assignments can be made: $1A_1$ at 2123



cm^{-1} , B_1 at 2029 cm^{-1} , $2A_1$ at 2011 cm^{-1} , and B_2 at 1969 cm^{-1} . Analogous assignments can be made for the phen and dmb complexes.

Initial Excited State. The lowest-lying excited-state for most Re^I -carbonyl complexes is typically either a ${}^3\text{MLCT}$ or a ${}^3\text{LC}$ state. In some cases, the excited-state behavior is more complex, and mixed excited-state processes or photochemistry are observed.^{24,31}

Both ${}^3\text{MLCT}$ and ${}^3\text{LC}$ states can be readily identified by TRIR. For ${}^3\text{MLCT}$ states, $\nu(\text{CO})$ shifts to significantly higher energy ($>40 \text{ cm}^{-1}$) relative to the ground state.^{28,31} This is due to a decrease in electron density at the metal center, which decreases π -back-bonding between the metal and the CO ligand, and increases the strength of the CO bond. For ${}^3\text{LC}$ states, there is no net change in electron density at the metal center, but there is increased π -interaction between the ligand and CO via the metal center. The ligand is a slightly better electron donor in the excited state than in the ground state, and donates a small amount of electron density to CO through the metal, which decreases the energy of $\nu(\text{CO})$ slightly ($<10 \text{ cm}^{-1}$).^{28,32}

Small positive shifts (~ 10 – 20 cm^{-1}) have been observed by Stufkens and co-workers for the $\sigma\pi^*$ excited state of *fac*- $[\text{Re}(\text{benzyl})(\text{CO})_3(\text{Pr-DAB})]^+$ (Pr-DAB is *N,N'*-diisopropyl-1,4-diazobutadiene).^{26,33} Similar results have been obtained by Omberg and co-workers for *fac*- $[\text{Re}(\text{CO})_3(\text{dmb})(\text{OQD})]^+$ (OQD is 1-methyl-6-oxyquinone).³⁴ The small positive shifts are consistent with depopulation of the Re^I -Pr-DAB or Re^I -OQD σ bond, and population of an excited state with the excited electron localized on the ligand. The decrease in electron density at the metal center decreases Re -CO back-bonding and increases the strength of the CO bond, though not as significantly as an MLCT state, where the observed shifts are much larger.

The TRIR spectra exhibited by the $[\text{Re}(\text{LL})(\text{CO})_4]^+$ series are not consistent with those described above. In all three spectra, bands arising from $2A_1$, B_1 , and B_2 modes shift slightly to higher energy (3 – 5 cm^{-1}), while the band arising from $1A_1$ shifts slightly to lower energy (5 – 10 cm^{-1}). Strouse and co-workers have assigned the lowest-lying excited state of $[\text{Re}(\text{LL})(\text{CO})_4]^+$ as an admixture of 1–3% MLCT character with

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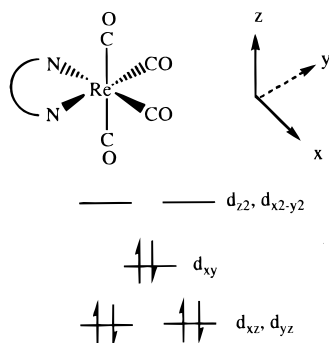
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an LC state by using low-temperature, single-crystal absorption.^{22,23} The best explanation of the TRIR spectrum concurs with this assignment. An LC state would shift the excited-state $\nu(\text{CO})$ bands to lower energy; for $[\text{Re}(\text{LL})(\text{CO})_4]^+$, however, this effect is counteracted by the MLCT character, which shifts the bands to higher energy.

To a first approximation, neglecting spin-orbit coupling, this can be understood in terms of the influence of the MLCT transition, which involves promotion of an electron from a d orbital in the plane of the polypyridine ligand to a π^* orbital perpendicular to that plane. This leaves a "hole" in the plane. The excited electron from the MLCT transition in the polypyridine π^* orbital can interact with the CO ligands via the metal center, as can the excited electron from the LC transition. Following the methods of Cotton and Kraihanzel,²⁹ the overall shifts of the bands can therefore be determined by the extent to which the modes interact with each state.

For the bands arising from the $2A_1$ and B_2 modes, the effect of the MLCT is large. The hole created by MLCT excitation is in the d_{xy} orbital; the axes and d orbital splitting are shown in the following diagram:



This hole is in the plane of the CO ligands involved in both the $2A_1$ and B_2 vibrations, and therefore the net shift for these bands is to higher energy. The $1A_1$ mode is least affected by the hole. It involves an in-phase vibration of the CO ligands that are out of the plane of the hole, and is only affected by mixing with the $2A_1$ mode. It is therefore shifted to lower energy. The B_1 mode, which involves the out-of-phase vibration of the out-of-plane ligands, is affected to an intermediate extent—less than the $2A_1$ and B_2 modes, but more than the $1A_1$ mode. Its net shift is slightly to higher energy. The larger shifts for the dmb complex are consistent with the greater degree of MLCT

admixture in the LC excited state. The increase in admixture increases the net shift.²³

CO Photodissociation. All three $[\text{Re}(\text{LL})(\text{CO})_4]^+$ complexes exhibit a long-lived excited state which undergoes photodissociation that can be observed in the TRIR spectra. As shown in Figure 5, for $[\text{Re}(\text{phen})(\text{CO})_4]^+$, initial excitation at 354.7 nm creates an excited state within the response time of the detector (<250 ns) which lives for several microseconds. Approximately $2 \mu\text{s}$ after the laser pulse, a photolysis product begins to appear. The photoproduct is formed with 100% efficiency as indicated by TRIR experiments using different flow rates. The TRIR spectrum (Figure 6) allows the identification of this product as a *fac*- $\text{Re}(\text{CO})_3$ solvento complex. The IR spectra of the product, which is stable within the time frame of the experiment, is similar to those of solvated 16-electron intermediates such as *fac*- $[\text{Re}(\text{LL})(\text{CO})_3(\text{DCE})]$ generated by photodissociation of CO ,^{22,23,35} indicating the solvated product is most likely formed as the result of photodissociation.

It is unlikely that photodissociation results from a largely LC excited state. It is more likely the result of the coupled, weakly photoactive $^3\text{MLCT}$ or a low-lying ligand field LF state. Previous studies of $[\text{Re}(\text{LL})(\text{CO})_4](\text{PF}_6)$ complexes have shown no evidence for a low-lying LF state, and have suggested that an LF pathway is unlikely because the CO ligands increase the energy of the $d\sigma^*$ orbitals.^{20–23} The decay trace observed by TRIR (Figure 5) shows monoexponential kinetics, consistent with photodissociation from the coupled $^3\text{MLCT}$ state.

Conclusion

TRIR measurements offer the unique opportunity to directly probe the excited-state dynamics of $[\text{Re}(\text{LL})(\text{CO})_4]^+$. These materials exhibit unique excited-state behavior consistent with a reaction pathway for photodissociation arising from coupling of the MLCT state to the lowest-lying nominally-LC excited state. The observed shifts in the excited-state frequency of $\nu(\text{CO})$ can be described in terms of MLCT contributions to molecular orbital overlaps in the $[\text{Re}(\text{LL})(\text{CO})_4]^+$ systems.

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