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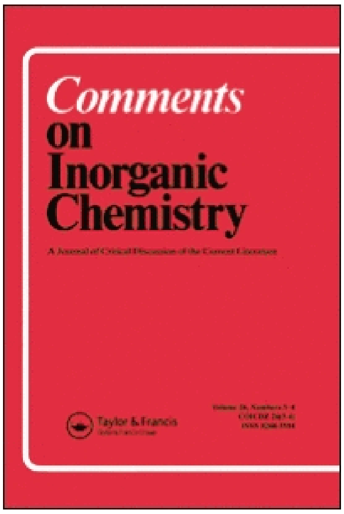

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Time-Resolved, Step-Scan FTIR Spectroscopy of Excited States of Transition Metal Complexes

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Time-Resolved, Step-Scan FTIR Spectroscopy of Excited States of Transition Metal Complexes

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Time-resolved, step-scan Fourier transform infrared spectroscopy has been developed as a method of studying electronically excited states of transition metal complexes. The technique takes advantage of the unique properties of carbonyl and cyanide stretching vibrations, including high infrared oscillator strength and well established sensitivity of vibrational frequency, intensity, and bandwidth to electronic and molecular structure. Electronic excitation generally produces significant transient infrared absorption changes which are characteristic of the changes in electronic structure, such as oxidation of the metal. TRIR spectroscopy thus provides new insight on the nature of the excited state transition (e.g. charge transfer vs. ligand centered), the extent of charge transfer, communication between metal centers, and energy and electron transfer processes. The step-scan FTIR approach has significant advantages over conventional time-resolved techniques, including spectral multiplexing, increased IR throughput, and fast data acquisition, making it possible to rapidly obtain complete spectra with good sensitivity and time-resolution.

Key Words: *time-resolved infrared spectroscopy, step-scan Fourier transform infrared spectroscopy, excited states*

Abbreviations: *FTIR—Fourier transform infrared LC—ligand centered MCT—mercury cadmium telluride CT—charge transfer TRIR—time-resolved infrared bpy—2,2′-bipyridine MLCT—metal-to-ligand charge transfer phen—1,10-phenanthroline*

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INTRODUCTION

Time-resolved infrared (TRIR) spectroscopy has become an important tool for the characterization of the excited states of transition metal complexes.[1–4] TRIR spectroscopy complements the more often utilized transient resonance Raman method, frequently providing unique information on the molecular vibrations, and hence unique insight into the structure and reactivity of short-lived chemical species.[2a,c] TRIR spectroscopy is particularly useful for characterizing excited states of transition metal complexes containing CO, CN, or other small ligands, which act as reporter groups of the electron and energy distribution within the complex.[1,2] The observables in the mid-IR spectra of these ligands are connected to molecular structure in well established ways; in particular, the number of modes and the mode coupling are both determined by the symmetry of the molecule, and the frequency and intensity of the vibrations are strongly dependent on the electronic structure.

Metal carbonyl complexes exhibit strong ν(CO) bands in the region between 1800 and 2200 cm^{-1}. The frequency of ν(CO) is generally shifted down when bound to a metal center compared to free CO. Upon binding to a metal, CO donates 5σ electrons to an empty orbital on the metal to form a σ-bond. A π-bond is also formed by donation of $d\pi$ electrons of the metal to an antibonding ($2p\pi^*$) orbital on the CO (π-backbonding). The shift to lower frequency upon bond formation is due to this π-backbonding, which weakens the CO bond. Any excited state process which produces a transient increase in electron density at the metal therefore causes a decrease in the CO stretching frequency; conversely, an increase in oxidation state at the metal results in ν(CO) at higher energy. The ν(CN) of free CN^- in aqueous solution is 2080 cm^{-1}. CN^- is a better σ-donor and poorer π-acceptor than CO. The net effect of coordination to a metal is to shift ν(CN) to higher energy, generally in the region of 2100 to 2200 cm^{-1}. Analogous to the carbonyl complexes, more electron density at the metal results in a decrease in ν(CN), whereas a higher oxidation state at the metal yields a higher value for ν(CN). The magnitude and direction of transient shifts in ν(CO) and ν(CN) induced by electronic excitation thus provide information on the orbital origin of the excited state, the oxidation state of the metal, and the extent of π-backbonding.

The structural specificity of TRIR is particularly useful in the case of polynuclear complexes which have the added complexity of excited state electron or energy transfer between metal centers. The electronic absorbance and emission spectra of these complexes consist of broad overlapping bands, making excited state processes such as electron transfer extremely difficult to sort out by conventional approaches. In contrast, the CO and CN stretching bands in the IR are diagnostic of the distribution of electrons and energy within the complex and the extent of communication between metal centers.[2]

Continuing advances in TRIR techniques have made it possible to measure infrared transients produced by laser excitation on any time scale (10^{-13}–10^{-3} s), throughout the mid-infrared (4000–500 cm^{-1}) and with high sensitivity ($\Delta OD < 10^{-4}$).[5,6] The sensitivity and time resolution of TRIR techniques are thus sufficient to follow even the most fundamental processes such as bond breakage and formation, and energy and electron transfer in complex molecular systems. One of the most significant advances in TRIR spectroscopy on the nanosecond and slower time scale has been the development of Fourier transform infrared (FTIR) as a time-resolved technique.[7,8] Conventional approaches to TRIR have relied on a monochromatic IR probe to obtain spectra a single wavelength at a time. The most widely employed method uses a tunable laser as the IR probe to obtain the kinetic IR response at each wavelength of interest. Spectra are then built up by obtaining successive transients throughout the spectral region of interest. This approach has been successfully applied to the study of excited states of transition metal complexes and to ligand binding dynamics in metalloproteins.[1,2,5] A related approach based on a dispersive scanning spectrometer has recently been described.[9] This system was shown to be capable of measuring transient signals in the microsecond to 50 nanosecond time frame with absorbance changes on the order of 10^{-5}. These measurements are also made at single wavelengths using monochromatic globar light, at the sacrifice of information elsewhere in the IR spectrum. Other problems associated with the conventional, single-wavelength approach include relatively long acquisition times required for a complete spectrum, reproducibility problems in intensity measurements over the spectral region, and the large amount of sample necessary. This can turn a TRIR experiment into an extremely tedious fishing expedition in search of the right wavelength(s) to observe the dynamics of interest, unless the appropriate wavelengths are known ahead of the fact. In contrast, time-resolved FTIR has the significant advantages of spectral multiplexing, increased IR throughput, and fast data acquisition, making it possible to rapidly obtain complete spectra with good sensitivity and time-resolution.

Several specific approaches to time-resolved FTIR have appeared within the last decade, the most useful being time-resolved step-scan FTIR.[7,8] A step-scan interferometer allows the moving mirror to be held at a fixed position while a transient is repetitively produced in the sample, for example with pulsed laser excitation. The moving mirror is then stepped to the next position and the process repeated. A temporally digitized reaction transient is thus obtained precisely synchronized with each discrete mirror position. The temporal resolution is determined by the detector response and the digitization process. The spectral resolution and free spectral range are determined by the number and interval of interferometer mirror steps. These data are reorganized by the FTIR control computer to yield a series of interferograms at a sequence of times. These are Fourier transformed into the time-resolved IR spectra, yielding a complete two-dimensional picture of the temporal evolution of the infrared spectrum. In this article, we describe the development of time-resolved step-scan FTIR as a powerful tool for the characterization of excited states of transition metal complexes.

STEP-SCAN FTIR METHODS

Commercial step-scan instruments are available, but generally require significant modifications for time-resolved applications. The three primary considerations for adapting commercial instrumentation to time-resolved applications are: (1) optical overlap of the infrared and pump laser beams; (2) the timing of the pump laser, the mirror stepping and the data acquisition; and (3) the dither signal some systems use for positioning the moving mirror. Efficient pumping of an excited state process requires tight focusing and careful overlap of the pump and probe beams, preferably in a collinear geometry to minimize photothermal artifacts. This is difficult to accomplish with a standard FTIR bench, which lacks a tight focus of the IR beam and has limited space for control of the pump beam. Synchronization of the pump laser with the stepping of the interferometer may require external electronics such as a digital delay generator; for example, if a Q-switched laser is used, timing pulses are required to fire the lamps and the Q-switch, with appropriate delays to properly position the laser firing within the step period. Allowances must be made for mechanical settling of the mirror and electronic settling of the detector amplifier. In addition, data acquisition must be synchronized to the laser and to the interferometer stepping. Finally, some commercial step-scan instruments dither the moving mirror to provide feedback control for mirror positioning. Unfortunately, this dither produces an infrared transient (at the fixed frequency of the dither) which has a large amplitude compared to that of a typical laser-induced transient. The dither transient acts as a significant noise source unless it can be demodulated from the transient of interest. This requires precise control of the phase of the laser firing and data collection relative to the phase of the dither signal.

We have modified a commercially available step-scan FTIR to produce an instrument capable of 250 nanosecond time resolution with sub-milli OD sensitivity. The optical arrangement is optimized using an external optical train, as shown in Fig. 1. A BioRad FTS 60A/896 serves as the step-scan interferometer. The IR beam from the interferometer is directed out of a sampling port of the interferometer to a mirror (M1) which directs the light to lens L1. This lens tightly focuses (300–1000 μm spot diameter) the IR light onto the sample. The pump beam is either made collinear with the probe using a dichroic mirror, or brought in at a small angle to the probe beam (Fig. 1). We use a Q-switched Nd:YAG laser operating at 10 Hz as the pump source. Alignment of the pump and probe beams is accomplished by operating the interferometer in the rapid scan mode and overlapping the two with a pin hole in place of the sample. The IR light is collected by lens L2 and focused by L3 onto the element of a photoconductive mercury cadmium telluride detector (Graseby Infrared). The rise time of the detector is approximately 250 ns. A low-pass germanium optical filter at 2250 cm^{-1} is attached to the face of the MCT detector for most of the transition metal complex experiments, both to block visible or NIR emission from the sample and to increase the dynamic range of the detector by filtering IR light outside the region of interest. This filter coupled with the CaF_2 cell windows and optics (high-pass 1250 cm^{-1}) yields a free spectral range of 1250 to 2250 cm^{-1}. The optical system is contained in a Plexiglas enclosure purged with dry nitrogen.

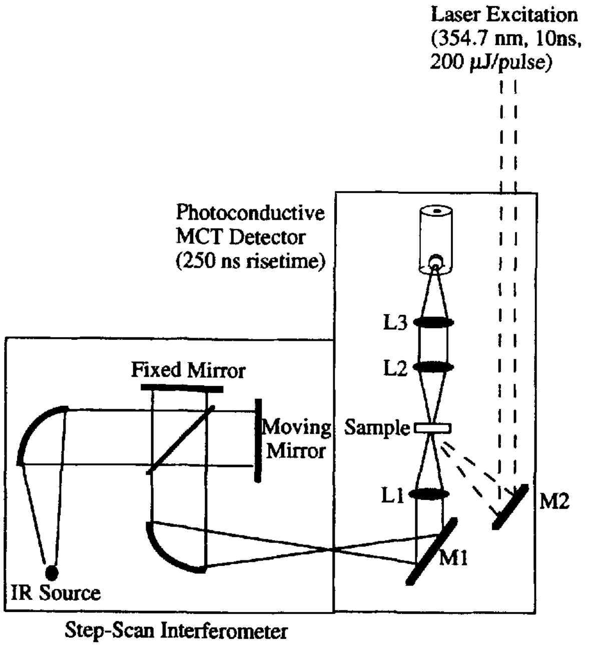


FIGURE 1 Optical arrangement of a time-resolved step-scan FTIR experimental setup, as described in the Introduction.

The precise synchronization of the interferometer stepping, the laser firing and the data acquisition is accomplished using a digital delay generator (Stanford Research Systems Model DG 535) with very small phase jitter (< 0.5 ns). The timing sequence is critical and thus requires the accuracy and stability of the digital delay generator. The interferometer serves as the master clock. It is stepped at 10 Hz and the delay generator is triggered at the beginning of each step cycle. Following appropriate delays to allow mechanical and electronic settling of the interferometer and detector, timing signals are provided for firing the flashlamps and Q-switch of the laser. The signal from the MCT detector is amplified by a dc-coupled preamplifier (2 MHz bandwidth) and processed in two matched boxcar integrators (Stanford Research Systems Model SR250). One gate is placed at time zero (defined as the start of the laser pulse) while the other is placed exactly 62.5 microseconds before time zero. This exact timing sequence is necessary to synchronize the phase of the 16 kHz moving mirror dither with the data acquisition. The two gates produce "dark" and "light" single beam spectra precisely in phase with the dither signal. The transient difference spectrum is computed as $\Delta A = -\log$ ("light"/"dark"), effectively demodulating the dither signal from the resulting difference spectrum.

We use the boxcar integrators not only to deconvolve the dither signal from the signal of interest, but also to achieve faster time resolution. The time resolution that can be achieved using the internal FTIR electronics is 5 μs, limited by the digitization rate (200 kHz) of the A/D converter. The time resolution using the boxcar integrators is determined by the convolution of the gate width of the integrator with the detector/amplifier response function. In principle, we can achieve 10 ns time resolution with this approach, using a photovoltaic MCT with a 10 ns rise time (Kolmar), a 10 ns boxcar gate width and a 10 ns Q-switched excitation pulse. In practice, however, the decreased sensitivity of the fast detector, coupled with increased $1/f$ and photon statistical noise severely limit the signal-to-noise of measurements on this time scale. We have found that 250 ns is the practical limit for detecting signals on the order of 0.5 milli OD (using a slower, more sensitive detector and a longer integration time) with reasonable acquisition times (~4 hours). The spectra reported in this work were obtained with a 600 ns integration time, generally with an average of 16 scans at 4 cm^{-1} resolution and a free spectral range of 3850 cm^{-1}, requiring 2233 steps per scan (one laser shot per step), or about 1 hour of collection time.

The ability to tightly focus the pump beam allows for laser power of between 100 and 300 μJ per pulse at the sample. At these low laser powers, sample integrity is ensured for the duration of the experiment (~36,000 laser shots) and for most samples no type of flow system is necessary, providing the additional advantage of smaller sample volumes. Sample concentration is dependent on the spectral region of interest. To examine carbonyl or cyano stretches, concentrations on the order of 1 mM are necessary (optical density of ca. 1 for ν(CO)). To interrogate IR absorption bands with smaller oscillator strength, higher concentrations are needed. Samples are deoxygenated by bubbling nitrogen or argon for at least 15 minutes. The sample is then transferred to a gas tight IR cell (1 mm pathlength) under an inert atmosphere.

TIME-RESOLVED SSFTIR STUDIES OF MONONUCLEAR COMPLEXES

***fac*-$Re^I(CO)_3$ Complexes.** Complexes of the type *fac*-$[Re^I(bpy)(CO)_3L]^{n+}$ (bpy = 2,2′-bipyridine or another polypyridyl ligand; L = halide, CN, or pyridine) are ideal systems for the application of time-resolved infrared spectroscopy. These complexes possess strong carbonyl stretches in the 1900–2050 cm^{-1} region, relatively long-lived electronically excited states, and have the added advantage of established synthetic chemistry.[10] Additionally, polypyridyl complexes of Re(I) play an increasingly important role in studies involving photochemical electron and energy transfer processes.[10–12] Since the initial studies of Wrighton and Morse,[10a] these complexes have continued to be important components in research associated with (1) the fundamental photophysics of metal-to-ligand charge transfer (MLCT) excited states (nonradiative decay; the Marcus "inverted" region),[10e,11d,13] (2) medium effects,[14] and (3) polynuclear systems such as chromophore–quencher complexes capable of long-range electron and energy transfer.[15] Furthermore, there is a complex interplay between MLCT and ligand-based excited states in these molecules.[16] The question of the excited-state electronic structure in these systems can be directly addressed by employing time-resolved infrared spectroscopy based on the step-scan FTIR technique.

Two carbonyls of *fac*-$[Re^I(bpy)(CO)_3L]^{n+}$ complexes are trans to the polypyridine ligand and one carbonyl is cis. These complexes can be considered effective C_{3v} or C_s symmetry, depending upon the identity of the L ligand. With L = pyridine (pseudo C_{3v}), two ν(CO) bands (A_1 + E) are evident in the FTIR spectrum (the band at lower frequency is broad, suggesting that the modes are not exactly degenerate), whereas with L = Cl (C_s), three resolved CO stretches (2A′ + A″) are observed. In either case, the CO stretch associated with the CO cis to the polypyridine ligand has been assigned to the higher frequency band.[1,17]

The step-scan FTIR difference spectrum of *fac*-$[Re^I(phen)(CO)_3(4\text{-methylpyridine})]^+$ (**1**) (phen is 1,10-phenanthroline) in Fig. 2 exhibits relatively large shifts to higher energy of both ν(CO) bands. The broad ground-state ν(CO) at 1931 cm^{-1} splits and shifts to higher energy with new bands appearing at 1962 and 2011 cm^{-1}. The ground-state band at

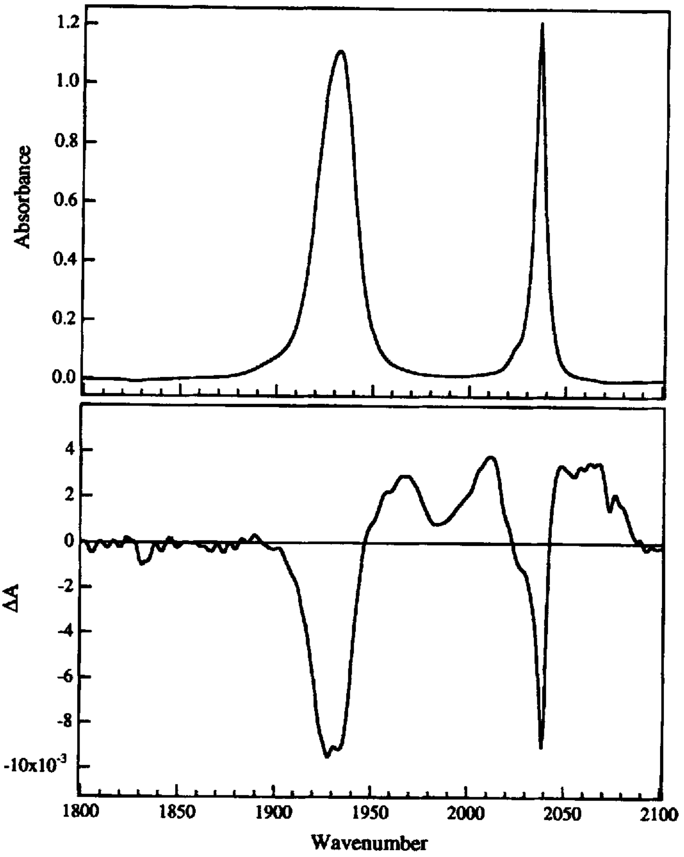
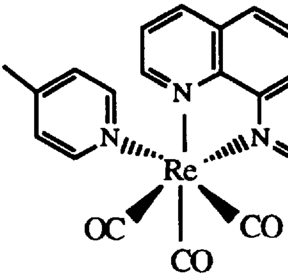


FIGURE 2 FTIR spectrum (top) and time-resolved, step-scan FTIR difference spectrum (bottom) of *fac*-[Re^I(phen)(CO)$_3$(4-methylpyridine)]$^+$) (phen is 1,10-phenanthroline) in CH_3CN at room temperature 600 ns after 354.7 nm (100–200 μJ/pulse, 10 ns) excitation, 4 cm^{-1} resolution and 16 co-added scans. The sample concentration is 1 mM in a 1 mm path length cell

2036 shifts to 2062 cm^{-1}. Similar spectra have been obtained for related Re^I(CO)$_3$ systems by kinetic IR measurements taken point-by-point through this spectral region; for example, the TRIR difference spectrum of *fac*-[Re^I(bpy)(CO)$_3$(4-ethylpyridine)]$^+$, shows ground-state bleaches at 1931 and 2036 cm^{-1} and transient absorbances at 1988, 2015, and 2075 cm^{-1}.[17] TRIR difference spectra of *fac*-[Re^I(4,4′-bpy)$_2$(CO)$_3$Cl]

(4,4′-bpy is 4,4-bipyridine) show ground-state depletion signals at 1891, 1936, and 2027 cm^{-1} and excited-state signals at 1957, 1992, and 2055 cm^{-1}.[1,18]



(1)

Large shifts to higher energy are expected for an MLCT excited state in which Re(I) is formally oxidized to Re(II):

$$fac\text{-}[\mathrm{Re^{I}(phen)(CO)_3(4\text{-}Mepy)}]^{+} \rightarrow$$

$$fac\text{-}[\mathrm{Re^{II}(phen\cdot^{-})(CO)_3(4\text{-}Mepy)}]^{+*}$$

The data clearly indicate a decrease in π-backbonding due to the oxidation of the Re and a concomitant shortening of the CO bond length. Attempts have been made to quantitate the change in CO bond length based on the change in vibrational frequency.[1] It is also possible to derive information on the orbital origin of the transition from the excited state spectrum. The CO bands are each shifted a different degree in the excited state; one of the CO bands associated with the carbonyls trans to the polypyridyl ligand is shifted much more strongly than the other one, resulting in the splitting of the ground state band. In addition, the cis CO band is shifted less than either of the trans (Table I). These observations support a localized hole in the dπ orbital configuration in the excited state (the dπ orbitals are fully occupied in the d^6 ground state). The excited state geometry must be significantly distorted from the pseudo C_{3v} ground state, such that one of the trans carbonyls interacts much more strongly with the excited state hole than the other. Finally, significant differences exist in the magnitude of shifts in the carbonyl stretches with different polypyridyl ligands. The general trend is bpy > 4,4′-bpy > phen as shown in Table I.

TABLE I

Excited state shifts† in ν(CO) for polypyridyl complexes of $Re^I(CO)_3$.

Complex	Δ_1	Δ_2	Δ_3
$Re^I(phen)(CO)_3(4\text{-}Mepy)$	31	80	26
$Re^I(4,4'\text{-}bpy)_2(CO)_3Cl$	56	66	28
$Re^I(bpy)(CO)_3(4\text{-}ethylpyridine)$	57	84	39

†Δ_1 and Δ_2 are the shifts of the trans carbonyls and Δ_3 is the shift of the cis carbonyl.

It should be possible to quantitate the degree of charge transfer in a series of closely related polypyridyl complexes of $Re^I(CO)_3$ with this approach.

Similar shifts to higher energy are noted with MLCT excitation of Os(II) complexes containing CO ligands. The transient difference spectrum of $[Os(tpy)(bpy)CO]^{2+}$ (tpy is 2,2′:6′,2‴-terpyridine) in CH_3CN measured with the step-scan technique shows a shift of 70 cm^{-1} of the CO band, from 1974 to 2044 cm^{-1}. This compares to shifts of 73 cm^{-1} for $[Os(phen)_2COCl]^+$ and 69 cm^{-1} for $[Os(bpy)_2CO(pyridine)]^{2+}$.[19]

The step-scan difference spectrum for *fac*-$[Re(dppz)(CO)_3(PPh_3)]^+$ (**2**) is shown in Fig. 3. In contrast to the large shifts evident for an MLCT excited state, the time-resolved infrared spectrum indicates that the ν(CO) bands are shifted only slightly in the excited state, and significantly, the shifts are to *lower* energy. The transient difference spectrum can be interpreted as three ground and three excited-state bands with the excited-state bands shifted ca. 8 cm^{-1} to lower energy and broadened by about a factor of 2 compared to the ground state. The large shifts to higher energy for *fac*-$[Re(phen)(CO)_3(4\text{-}Mepy)]^+$ are expected for a lowest lying MLCT excited state in which Re(I) is formally oxidized to Re(II), whereas the small shifts for *fac*-$[Re(dppz)(CO)_3(PPh_3)]^+$ are consistent with a lowest, ligand-localized excited state, Re(I)-$^3\pi\pi^*$(dppz). The slight shift of ν(CO) to lower energy is due to the greater extension of the π^*(dppz) orbitals and therefore better overlap with the metal dπ orbitals, resulting in an increase in electron density on the metal. As previously noted, increased electron density on the metal yields increased π-backbonding with CO causing a decrease in the CO stretching frequency.

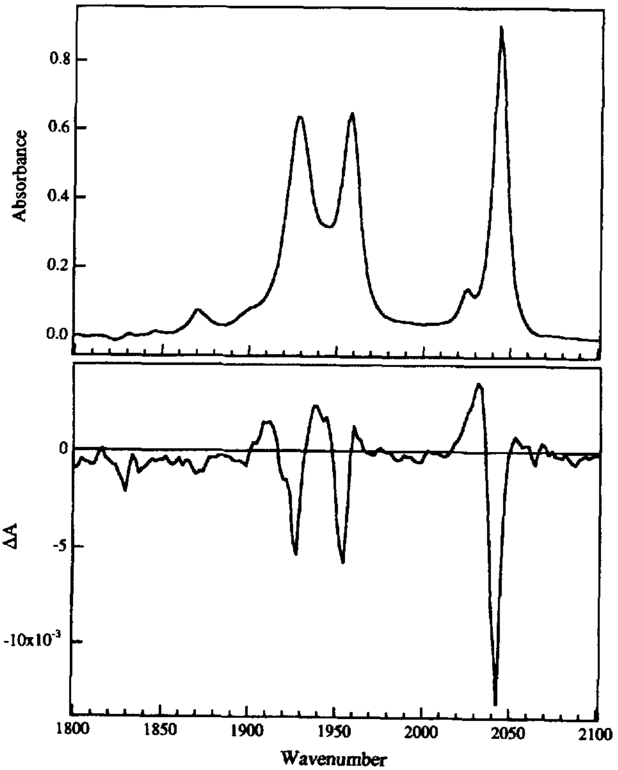
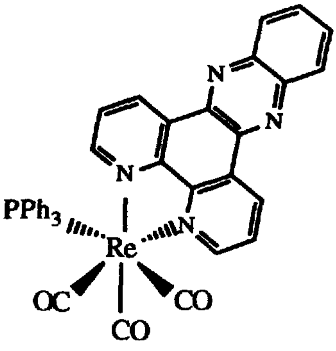


FIGURE 3 FTIR spectrum (top) and time-resolved, step-scan FTIR difference spectrum (bottom) of *fac*-[Re(dppz)(CO)$_3$(PPh$_3$)]$^+$ (dppz is dipyrido[3,2-a:2′,2′-c]phenazine; PPh$_3$ is triphenylphosphine). Experimental conditions are as described in Fig. 2.



(2)

The step-scan FTIR approach is particularly valuable for more complex systems such as *fac*-[Re(4,4′-$(NH_2)_2$)-bpy)$(CO)_3$(4-Etpy)]$^+$ (3) (4,4′-$(NH_2)_2$)-bpy is 4,4′-diamino-2,2′-bipyridine; 4-Etpy is 4-ethylpyridine), which have the possibility of simultaneous population of multiple excited states. The step-scan difference spectrum for *fac*-[Re(4,4′-$(NH_2)_2$)-bpy)$(CO)_3$(4-Etpy)]$^+$ (Fig. 4) demonstrates features that can be attributed to an MLCT excited state and at least one addi-

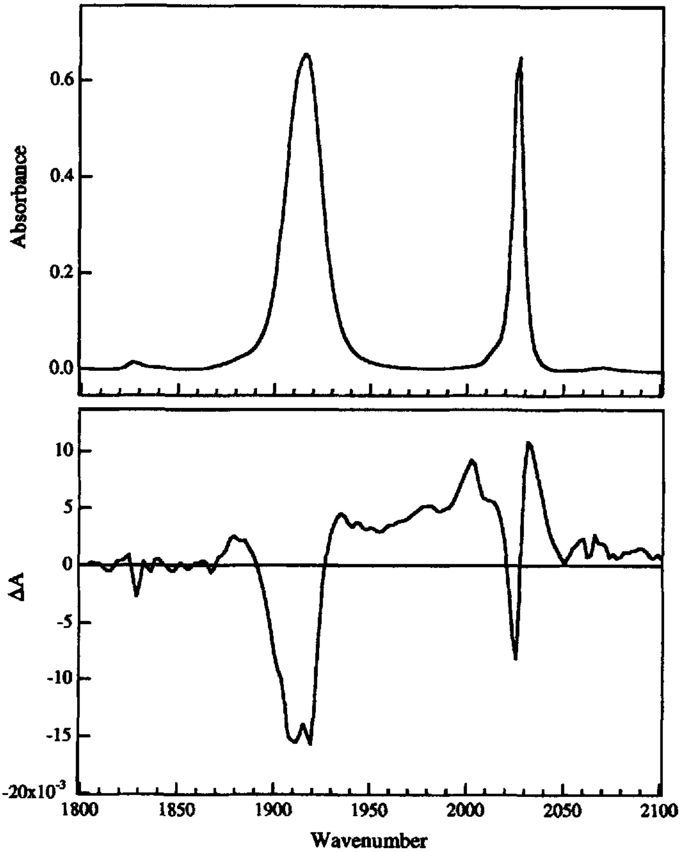
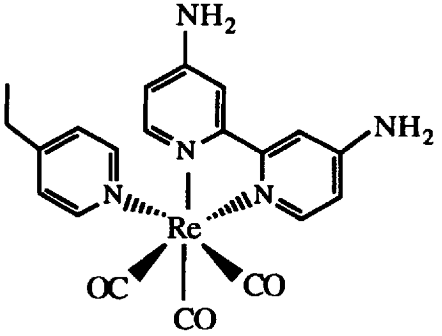


FIGURE 4 FTIR spectrum (top) and time-resolved, step-scan FTIR difference spectrum (bottom) of *fac*-[Re(4,4′-$(NH_2)_2$)-bpy)$(CO)_3$(4-Etpy)]$^+$ (bottom, 4,4′-$(NH_2)_2$)-bpy is 4,4′-diamino-2,2′-bipyridine) in CH_3CN at room temperature 600 ns after 354.7 nm (100 μJ/pulse, 10 ns) excitation. The transient spectrum is the result of 64 co-added scans.

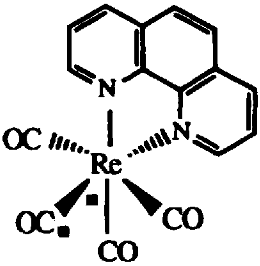
tional, ligand-based state. The positive shifts in ν(CO) from the ground state at 1914 and 2025 cm^{-1} to 1979, 2002 and 2064 cm^{-1} are comparable to those observed for a MLCT excited state. A set of bands is also observed shifted to lower energy at 1881 and 2014 cm^{-1}, comparable to the shifts observed for the ππ* state of the dppz complex. Spectral simulation provides evidence for a third set of excited-state bands at 1930 and 2031 cm^{-1}, consistent with population of perhaps a ligand centered *n*π* state. The time-resolved infrared spectrum therefore provides conclusive evidence for the concurrent population of multiple excited states in fluid solution. This possibility had been suggested previously based on the electronic spectroscopy of this complex.[20] UV-visible excitation in fluid solution results in the appearance of a characteristic MLCT emission with λ_{max} = 570 nm. Transient UV-visible absorption difference spectra also suggest population of both a ligand-localized excited state (or states), with a broad absorption feature at 450 nm, and an MLCT excited state with a radical π → π* (4,4′-$(NH_2)_2$)-bpy·-) absorption band appearing at 370 nm; however, the bleaches expected for the MLCT and π → π* transitions are not observed. These examples demonstrate the exquisite sensitivity of the CO transitions to the electron distribution in such complexes and therefore the utility of the step-scan FTIR method for definitive characterization of the excited states.



(3)

Re^{I}(CO)$_4$ Complexes. The class of Re(I) carbonyl complexes of the type $[Re(CO)_4(LL)]^+$ (LL is bpy or phen) exhibit unique excited state behavior; the best description of the excited state based on electronic spectroscopy is nominally ligand centered (LC) with an admixture of 1–3% charge transfer (CT) character.[21] Mixing between the ^{3}LC and ^{1}CT states results in metal-ligand sidebands in the absorption spectrum and a line-narrowed luminescence spectrum having a short luminescence lifetime for the ^{3}LC state. Furthermore, in the single crystal absorption spectrum of $[Re(bpy)(CO)_4](PF_6)$, splitting of the ^{3}LC into the three triplet sublevels is observed and the transition dipole for the ^{3}LC is along the Re → N bond, which is more typical for a CT excited state. The complexity and unusual nature of the excited state behavior of these complexes makes them ideal candidates for time-resolved infrared characterization.

The tetracarbonyl systems have C_{2v} symmetry with the C_2 axis defined as intersecting the Re center and the 2,2′-C-C bond of the bipyridyl type ligand. Consequently, there are four carbonyl vibrational modes for these molecules: an A_1 mode which is a linear combination of the in-phase motion of the trans carbonyls, the analogous A_1 mode involving the cis carbonyls, a B_1 mode for the out-of-phase motion of the cis carbonyls, and the analogous B_2 mode arising from the trans carbonyls. Since all four of these ν(CO) modes can be clearly distinguished in the infrared spectrum, they can be used to probe excited state changes with unique sensitivity to cis and trans effects.



(4)

In Fig. 5, the transient infrared spectrum is compared to the FTIR spectrum of $[Re(phen)(CO)_4(PF_6)$ (**4**) in 1,2-dichloroethane. The ground-state infrared assignments for ν(CO) are A_1 (cis) at 2122 cm^{-1}, A_1 (trans) at 2029 cm^{-1}, B_1 (cis) at 2010 cm^{-1} and B_2 (trans) at 1970 cm^{-1}. In the transient spectrum, shifts are noted to 1977 cm^{-1} (B_2), 2016 cm^{-1} (B_1) and 2035 (A_1). The transient infrared signal corresponding to the 2122 cm^{-1} mode is obscured by an intense solvent band. As expected for a LC state in

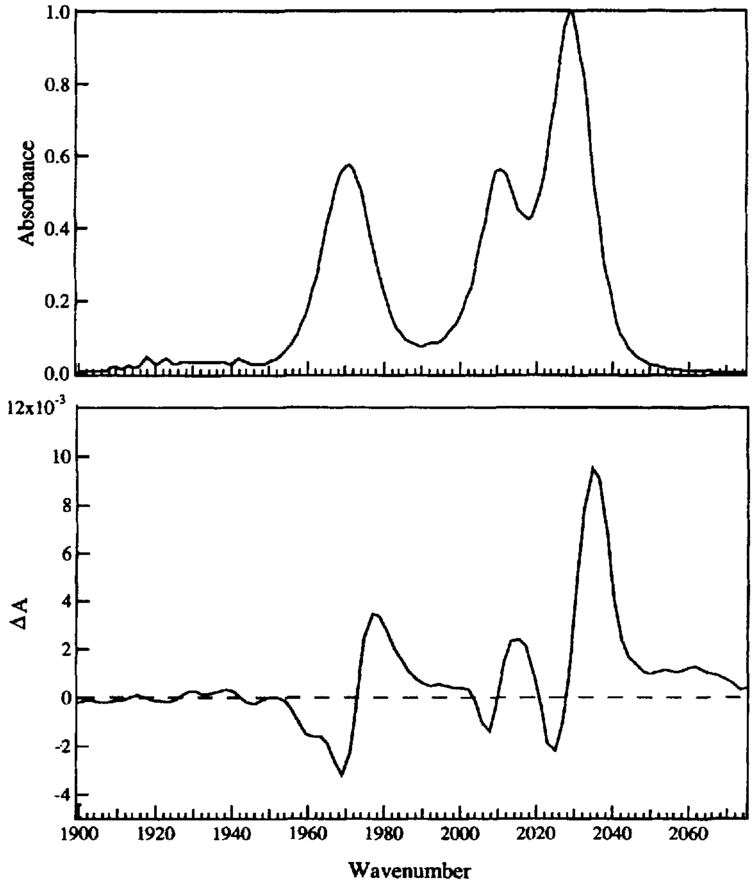


FIGURE 5 FTIR spectrum (top) and time-resolved, step-scan FTIR difference spectrum (bottom) of $[Re^{I}(phen)(CO)_4]^+$. Spectra were measured in dichloroethane at room temperature. Laser excitation was 354.7 nm (10 Hz, 10 ns, 100–200 μJ/pulse), 4 cm^{-1} resolution and 16 co-added scans.

which no formal change occurs in the oxidation of the metal, the shifts in ν(CO) are small for both the cis and trans carbonyls (~6 cm^{-1}). The shifts are to higher energy, however, contrary to the prediction for an LC state. Instead of an increase in the π-electron density at the metal due to population of the π* antibonding orbital of the phen ligand, the shifts to higher energy for the ν(CO) bands indicate a slight decrease, reminiscent of a CT state. This behavior corroborates the observations in the absorption and luminescence studies of a nominal LC state that has substantial CT character. The effect of the CT character is to cause a net positive shift of the ν(CO) arising from the net decrease in electron density at the metal center. Studies are continuing on $[Re(CO)_4(LL)]^+$ systems in order to correlate the observed transient infrared shifts with the degree of mixing of the LC and CT states.

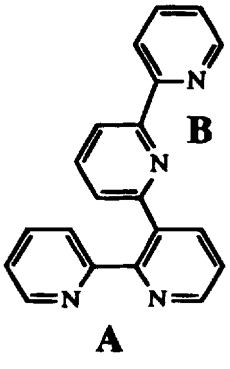
An important consequence of the C_{2v} symmetry of tetracarbonyl complexes is that the cis and trans carbonyl stretches have different symmetries and exhibit different polarizabilities. Consequently, we expect the behavior of the cis and trans carbonyls to provide additional insight into the electron distribution in the excited state. Interestingly, shifts observed for the cis and trans carbonyl modes of the excited state of **4** are identical, suggesting that the electron distribution is symmetric with respect to the carbonyls in this state. This observation is consistent with mixing of both d_{xz} and d_{yz}, but not d_{xy} orbitals in the ligand centered excited state, such that the charge transfer character of the excited state affects both the cis and trans carbonyls equivalently. The effect of reduced symmetry, such as site induced distortions in the solid state, is expected to provide additional insight into the nature of the excited states of this type of complex.

TIME-RESOLVED SSFTIR STUDIES OF POLYNUCLEAR COMPLEXES

A significant amount of photochemical research in the past several years has focused on the synthesis and study of polynuclear or supramolecular coordination compounds.[22] These systems consist of two or more transition metal subunits linked together by a suitable bridging ligand. The intercomponent photochemistry and photophysics (electron and energy transfer processes) of these polynuclear systems is an area of immense interest. The prevailing goal has been to control the intercomponent processes in these systems to achieve efficient light harvesting and charge separation. Photonic devices such as a photovoltaic cell based on supramolecular systems which act as sensitizers have already been demonstrated. Nevertheless, a detailed understanding of the photochemistry and photophysics of these systems is not generally available, largely due to the lack of specificity of conventional electronic spectroscopies. Time-resolved vibrational spectroscopies, including step-scan

FTIR, have already made a vital contribution to the characterization of the excited states of supramolecular systems.

One unique feature of supramolecular systems is the control over intercomponent processes provided by the bridging ligand, which can function not only as a structural link but also to modulate electron or energy transfer. The complex $[(bpy)_2Ru^{II}ABRe^{I}(CO)_3Cl]^{2+}$ (AB is 2,2′:3′2″:6″,2‴-quaterpyridine (**5**)), is an important example of control of the direction of energy transfer by the bridging ligand.[23] The asymmetric bridge (AB) contains two inequivalent metal binding sites, one more sterically hindered than the other. 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. However, the extent of perturbation of the MLCT energies, the direction of energy transfer and the nature of the relaxed excited state in each case is not clear.



(5)

We have characterized the relatively long lived (~400 ns) excited state of $[(bpy)_2Ru^{II}ABRe^{I}(CO)_3Cl]^{2+}$ in CH_3CN. The step-scan FTIR difference spectrum is shown in Fig. 6. The ν(CO) bands demonstrate a slight shift to lower energy following excitation. The band at 2023 cm^{-1} shifts to 2016, while the band at 1918 shifts to 1910 and the band at 1902 shifts to 1888. The magnitude and direction of these shifts are characteristic of a ligand centered $\pi\pi^*$ state, analogous to the changes observed in the spectrum of (**2**). We conclude that following initial excitation into

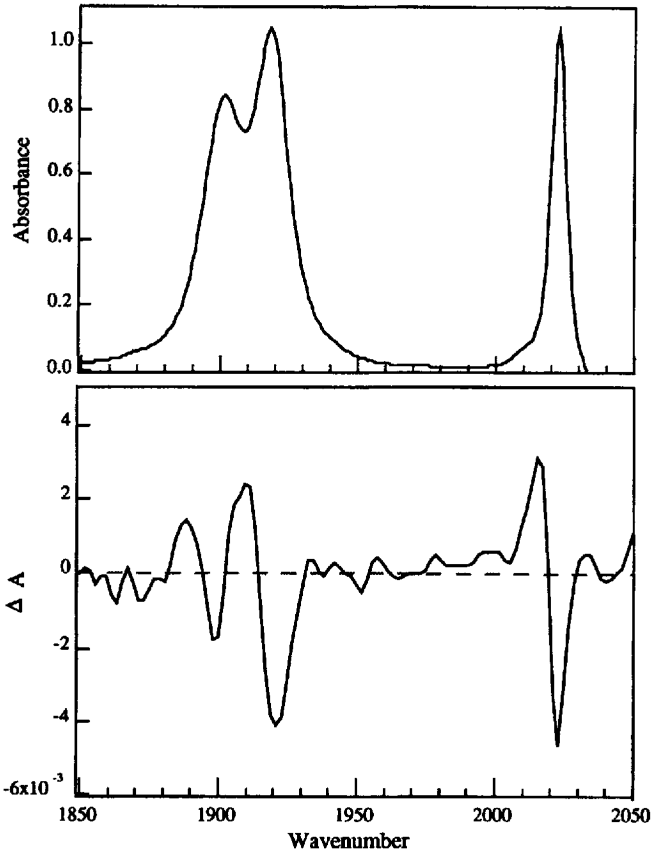


FIGURE 6 FTIR spectrum (top) and time-resolved, step-scan FTIR difference spectrum (bottom) of $[(bpy)_2Ru^{II}ABRe^{I}(CO)_3Cl]^{2+}$ (AB is 2,2′:3′2″:6″,2‴-quaterpyridine) in CH_3CN at room temperature. Experimental conditions were as described in Fig. 2.

MLCT transitions centered on the Re or the Ru, energy transfer occurs to give a $Ru^{II} \rightarrow AB$ MLCT state, best described as $[(bpy)_2Ru^{III}(AB^{-})Re^{I}(CO)_3Cl]^{2+*}$; this transient species lives for about 400 ns. The reduced AB bridge effectively increases the electron density on the Re, causing an increase in π-backbonding and a decrease in the CO stretching frequencies.

The cyano bridge is a common structural motif in supramolecular complexes. This simple bridge provides a mechanism for linking multiple metal centers together to construct a molecular wire for cascading energy or electron transport. The cyano bridged ReRu dimer $[(\mathrm{phen})(\mathrm{CO})_3\mathrm{Re}^{\mathrm{I}}(\mathrm{NC})\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_2(\mathrm{CN})]^+$ 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.[17] In the ground-state FTIR spectrum, bands are observed for the carbonyl and cyano stretches. Two ν(CO) bands are present as a broad band at 1927 cm^{-1} with a narrow band at 2028 cm^{-1}. Additionally, two ν(CN) stretches are observed at 2081 and 2100 cm^{-1}. The ν(CN) at 2081 cm^{-1} is assigned to the terminal cyanide while the higher energy stretch is attributed to the bridging cyanide.[24]

The step-scan FTIR difference spectrum of the dimer 500 ns after excitation of the $\mathrm{Re}^{\mathrm{I}} \rightarrow$ phen MLCT transition shows two derivative shapes associated with the carbonyl stretches and two bleaches for the cyanide stretches, one centered at 2079 cm^{-1} and the other at 2094 cm^{-1}. Two excited-state ν(CN) bands are observed at 2108 cm^{-1} and 2132 cm^{-1}, shifted by +29 and +38 cm^{-1}, respectively. In contrast, the excited-state ν(CO) bands at 1929 and 2030 cm^{-1} are shifted less than 2 cm^{-1} from the ground state. The large positive shifts of the cyanide stretches following excitation are consistent with oxidation of the Ru(II) to Ru(III). The small positive shifts of the ν(CO) bands suggest some electronic communication from the Ru(III) through the CN bridge. The 500 ns FTIR spectrum clearly indicates that energy transfer from the initially excited $\mathrm{Re}^{\mathrm{I}} \rightarrow$ phen MLCT state has already occurred on this time scale to produce a $\mathrm{Ru}^{\mathrm{II}} \rightarrow$ bpy MLCT state best described as $[(\mathrm{phen})(\mathrm{CO})_3\mathrm{Re}^{\mathrm{I}}(\mathrm{NC})\mathrm{Ru}^{\mathrm{III}}(\mathrm{bpy})(\mathrm{bpy}^{-})(\mathrm{CN})]^{+*}$.

The cyano bridge is also asymmetric, a property useful for controlling the direction of energy transfer. In addition, fine tuning of the donor and acceptor energy levels can be achieved by varying the ligands on the metal centers. Both of these concepts are illustrated with the complex $[(\mathrm{NC})(\mathrm{bpy})_2\mathrm{Ru}^{\mathrm{II}}(\mathrm{CN})\mathrm{Ru}^{\mathrm{II}}(\mathrm{phen})_2(\mathrm{CN})]^+$. $\mathrm{Ru}^{\mathrm{II}} \rightarrow$ bpy MLCT excitation of this complex in $\mathrm{CH_3CN}$ produces the step-scan FTIR difference spectrum shown in Fig. 7. The spectrum clearly shows three excited-state cyanide stretches at 2037, 2091, and 2104 cm^{-1}. The ground-state bleach of the terminal cyanides is observed at 2075 cm^{-1}, whereas the bleach for $\nu(\mathrm{CN})_{\mathrm{bridge}}$ is coincident with the two excited-state bands of the terminal

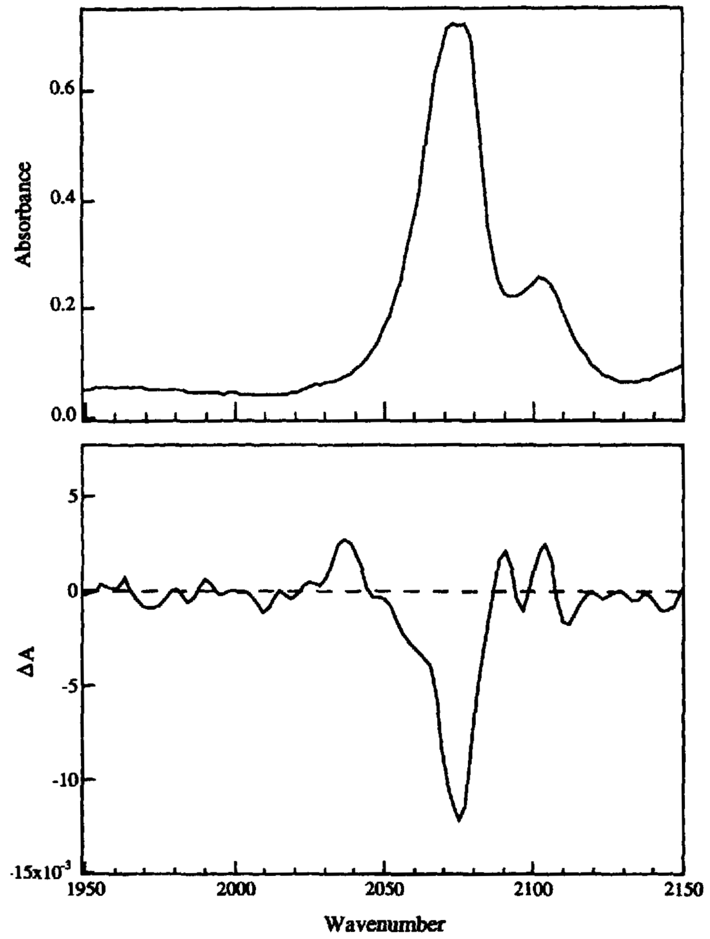


FIGURE 7 FTIR spectrum (top) and time-resolved, step-scan FTIR difference spectrum (bottom) of $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(phen)_2(CN)]^+$ measured in CH_3CN at room temperature. Excitation was 354.7 nm (200 μJ/pulse, 10 ns) with a concentration between 1 and 2 mM in a 1 mm path length cell.

cyanides. The transient IR data indicate that energy transfer occurs to the N-bonded chromophore of the cyano-bridge to yield $[(NC)(bpy)_2Ru^{II}(CN)Ru^{III}(phen^-)(phen)(CN)]^+$ as the predominant species present on the nanosecond time scale.[25]

SUMMARY

Step-scan FTIR is a relatively new technique that has already made a significant impact on the practice of time-resolved infrared spectroscopy. There are many advantages of this technique over conventional approaches to TRIR measurements. The main advantage is reduced spectral acquisition time. Adequate signal-to-noise is generally obtained with about one hour of signal averaging. Short acquisition time minimizes sample degradation due to heating or photochemistry, eliminating the need to flow most samples. Another significant benefit of the step-scan approach is the multiplex advantage, which we have exploited to obtain the complete spectrum in the CO and CN stretching regions. Furthermore, although the focus of this review has been on the 5 μm spectral region, the instrument is capable of capturing the entire time-resolved, mid-infrared spectrum. Vibrational modes arising from the polypyridyl ligands (1200–1600 cm^{-1}), for example, are accessible and should provide additional insight into the structure of the excited state. In principle, the time resolution of these measurements is limited only by infrared detector technology to about 10 ns; however, signal-to-noise considerations impose a practical limit of about 250 ns for most measurements. Technological improvements in detector response, optics and incoherent IR sources should push this time limit closer to 10 ns. Finally, commercially available step-scan FTIR spectrometers are readily adapted to time-resolved applications.

The rich detail of the vibrational spectrum offers new insight into fundamental photochemical and photophysical processes. We have exploited the sensitivity of the infrared modes of small ligands such as CO and CN to the distribution of electrons within a transition metal complex to characterize excited state structure. This approach has produced new information on the nature of the excited state transition (e.g., charge transfer vs. ligand centered), the extent of charge transfer, communication between metal centers and energy and electron transfer processes. We have taken advantage of only one dimension of this method, since we have ignored much of the infrared spectrum. Finally, widespread application of TRIR spectroscopy has been hindered by the difficulty of these experiments. We expect the ease of obtaining TRIR spectra via the step-scan FTIR technique, combined with the structural specificity of vibrational spectroscopy, to precipitate a revolution in the application of this technique to the study of excited state processes.

Acknowledgments

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