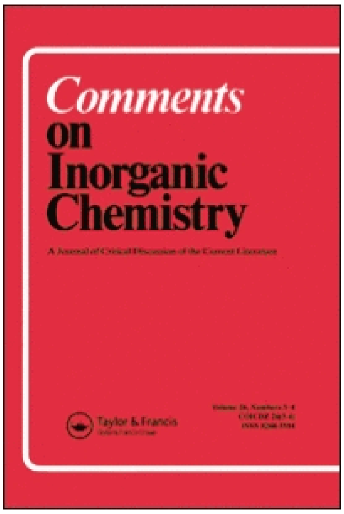


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Application of Time-Resolved Vibrational Spectroscopy to the Study of Excited-State Intercomponent Processes in Supramolecular Systems

Carlo A. Bignozzi[a]; Jon R. Schoonover[b]; R. Brian Dyer[b]
[a] Dipartimento di Chimica, Università di Ferrara, Ferrara, Italy [b] Los Alamos National Laboratory, Bioscience and Technology Group, Los Alamos, New Mexico

To cite this Article Bignozzi, Carlo A. , Schoonover, Jon R. and Dyer, R. Brian(1996) 'Application of Time-Resolved Vibrational Spectroscopy to the Study of Excited-State Intercomponent Processes in Supramolecular Systems', Comments on Inorganic Chemistry, 18: 2, 77 — 100

To link to this Article: DOI: 10.1080/02603599608032715

URL: http://dx.doi.org/10.1080/02603599608032715

Application of Time-Resolved Vibrational Spectroscopy to the Study of Excited-State Intercomponent Processes in Supramolecular Systems

CARLO A. BIGNOZZI
Dipartimento di Chimica,
Università di Ferrara,
Ferrara, Italy

JON R. SCHOONOVER and
R. BRIAN DYER
Bioscience and Technology Group,
Los Alamos National Laboratory,
Los Alamos, New Mexico 87545

Received July 28, 1995

The application of time-resolved vibrational (Raman and infrared) spectroscopy to the study of excited-state intercomponent processes in inorganic chemistry represents a powerful new application of these techniques. The development of vibrational spectroscopy with time resolution from microseconds to femtoseconds to characterize the photochemistry and photophysics of metal-containing supramolecular systems provides a mechanism for understanding the fundamental processes which occur following photolysis. The utility and potential of this approach in the elucidation of excited-state processes is demonstrated with studies of excited-state localization, excited-state structure, and photoinduced intramolecular electron and energy transfer.

Key Words: *supramolecular systems, polynuclear complexes, vibrational spectroscopy, excited states*

Comments Inorg. Chem
1996, Vol. 18, No. 2, pp. 77–100
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

1. INTRODUCTION

The spectroscopic studies of excited-state processes of inorganic systems have generally focused on transient emission and especially transient electronic absorption spectroscopy. The transient absorption method depends upon the appearance of characteristic absorption bands to define intermediate states. With the trend toward larger more complex supramolecular systems,[1] data interpretation becomes more complicated because electronic absorption features are typically broad and these systems can have several absorbing chromophores. Furthermore, detailed characterization of the structure of chemical transients following excitation is fundamental to the understanding of the excited state and subsequent electron and energy transfer processes. Electronic spectroscopy is limited in the amount of structural information it can provide.

Infrared and Raman spectroscopies with appropriate temporal resolution overcome these problems with the vibrational information offered in the resulting spectra. Resonance Raman and time-resolved resonance Raman spectroscopy have proven to be most useful in the study of excited states of inorganic complexes in solution.[2] Additionally, with the advent of the time-resolved infrared technique, transient infrared data may now be obtained on time scales ranging from microseconds to femtoseconds.[3] The utility and potential of these spectroscopic techniques in the elucidation of excited-state processes is discussed in the context of excited-state localization, excited-state structure, and photoinduced intramolecular electron and energy transfer.

2. INSTRUMENTATION

Time-resolved resonance Raman (TR^3) spectroscopy on the nanosecond time scale has been extensively utilized over the past 15 years. This experiment is conducted in one of two ways, depending upon the method of detection. With a typical scanning spectrometer/photomultiplier tube arrangement of the type used in continuous-wave (CW) resonance Raman spectroscopy, transient spectra can be measured using boxcar integration with a pulsed laser source. While this approach takes advantage of the dispersion and Rayleigh rejection capabilities of a scanning double monochromator, significant disadvantages exist in the time needed for a complete spectrum and the numerous excitation pulses needed in the course of the experiment.

Optical multi-channel analyzers (OMA's) and charge-coupled devices (CCD's) with a spectrograph provide the ability to measure a complete spectrum with a single laser pulse. This approach provides a significant advantage in the time needed to obtain a spectrum. With intensifiers on these devices, gated detection is possible. The intensifier can be "on" or "off" following the laser pulse for time resolution. The advantage to this approach is that a single laser pulse can be used to both excite the sample and as a source for the Raman scattering. Time resolution is limited by the laser pulse and the gate in this experiment so that the best time resolution with sufficient Raman signal is on the order of 50 ns.

The pump-probe approach can be used to provide better time resolution for the transient Raman experiment (Fig. 1). In this experiment, a laser pulse is used to excite the sample and a second laser pulse is used as a source for the Raman scattering. A CCD without an intensifier can be used for a detector. The time resolution is determined by the timing between the two pulses. The use of a picosecond laser system then allows for the study of very fast processes following excitation.

Continuing advances in transient infrared spectroscopy have led to the ability to measure transient IR signals following laser excitation on a variety of time scales.[3] Time-resolved infrared spectroscopy is complementary to the more often utilized transient resonance Raman method, and the combination of these two approaches represents the opportunity to gain insight into the entire vibrational nature of short-lived transient species.

In supramolecular photochemistry, transient infrared spectroscopy is particularly valuable in the study of complexes containing CO or CN^- because ν(CO) and ν(CN) have high oscillator strengths. The sensitivity of the frequencies and bandwidths of these vibrations to electronic and molecular structure is well established. Electronic excitation generally produces intense transient infrared absorption changes which are characteristic of the changes in electron density within the complex. Additionally, it is possible to obtain transient spectra throughout the mid-IR region which can supplement Raman results.

One approach to time-resolved infrared spectroscopy on the nanosecond time scale uses a monochromatic monitoring beam and a pulse of laser excitation source with transient signals being monitored point by point over the spectral region of interest.[3a] This experiment suffers from relatively long acquisition times required for a complete spectrum and

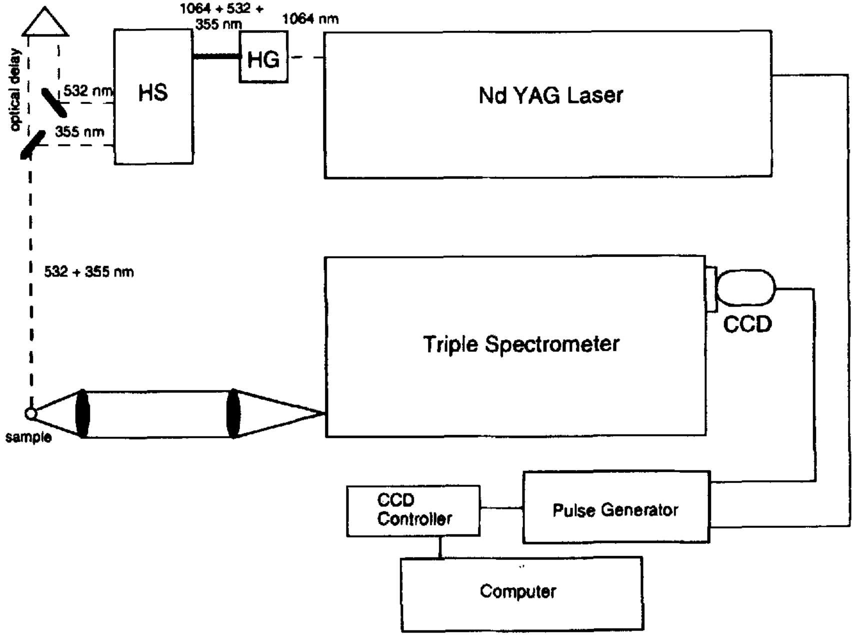


FIGURE 1 Two color (pump-probe) time-resolved resonance Raman apparatus. In this setup the fundamental of 1064 nm of a pulsed ND: YAG laser is frequency doubled and tripled to create pulses at the second and third harmonics (532 and 355 nm) in the harmonic generator (HG). The second and third harmonics are separated by a harmonic separator (HS) and the probe beam (532 nm) delayed in time. The pump and probe beams are overlapped and directed onto the sample. Raman scattering from the probe pulses are detected by a CCD attached to a triple monochromator. The timing of the experiment is accomplished with a pulse generator and the data acquisition and manipulation are controlled by a computer.

the need for a tunable IR source throughout the region of interest. While it is possible to obtain transient spectra with a dispersive instrument, a potentially valuable method uses step-scan Fourier transform interferometry.[3d,4] In this experiment laser excitation occurs at each mirror position and the transient signal is measured. An interferogram is created point by point at each mirror position with a single interferogram being recorded for Fourier transformation. Several interferograms can be collected for the needed signal-to-noise ratio.

Commercial instrumentation is available for some step-scan applications. We have modified a commercial system which is capable of nanosecond time resolution in the study of inorganic complexes and supramolecular systems (Fig. 2). This set-up can measure FTIR difference spectra for short-lived (nanosecond time scale) electronically excited states and related photochemistry. The apparatus uses a step-scan interferometer as the IR source, boxcar integration of a photovoltaic MCT detector, a stable timing scheme for data collection, and external optics for tightly focusing the IR beam on the sample and collecting the IR signal.

The pump-probe approach can also be used for time-resolved infrared spectroscopy, allowing for measurement of ultrafast IR spectra. One approach to ultrafast IR spectroscopy uses a short pump pulse and up-conversion of a CW IR signal with a second short visible pulse for visible detection.[5] This up-conversion experiment is very similar to an ultrafast visible experiment. A second experimental approach uses the generation of short IR pulses as the probe beam. Several methods are available for the generation of short IR pulses; one approach is shown in Fig. 3.

In this type of experiment, the probe beam is split into sample and reference beams before the sample and interrogated by a mid-IR sensitive detector. The ratio of sample to reference signal is then computed electronically. As with the nanosecond experiment on supramolecular systems, picosecond IR measurements have focused on metal carbonyl compounds because of the large IR absorption cross section. It should be possible, however, to extend these studies to other vibrational transitions.

3. EXCITED-STATE LOCALIZATION

One of the main applications of time-resolved resonance Raman spectroscopy has been in the investigation of the site of localization of the excited electron following photoexcitation in mixed-ligand metal com-

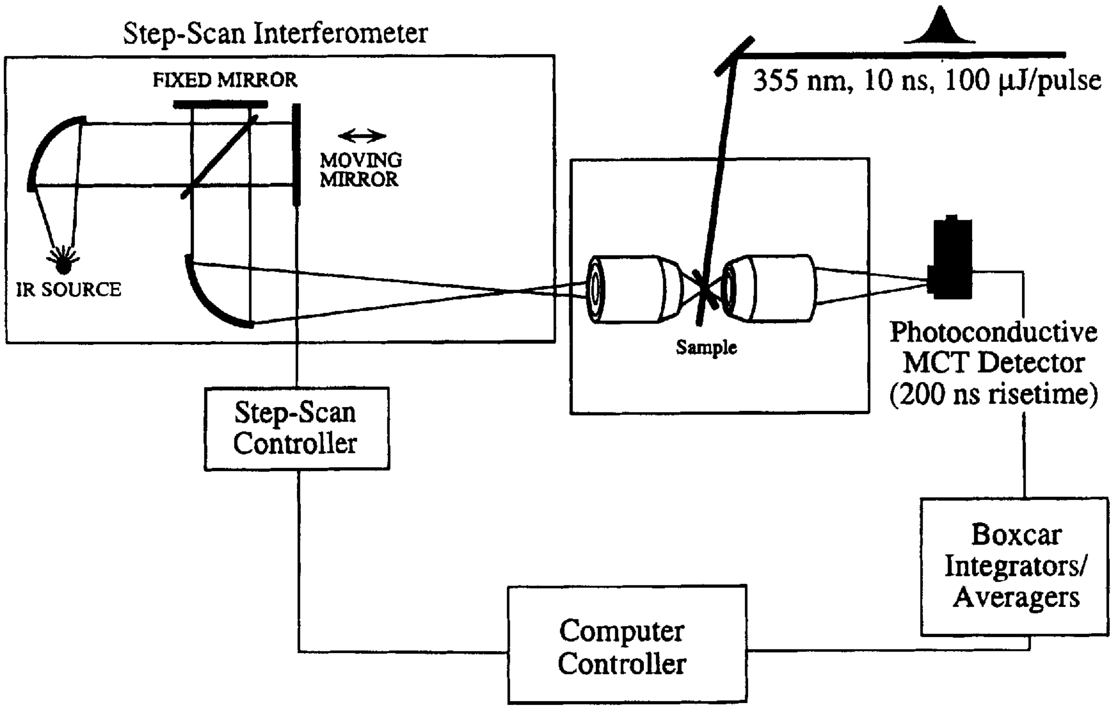


FIGURE 2 Time-resolved, step-scan FTIR apparatus for collection of FTIR difference spectra on the nanosecond time scale. The experiment is described in the text.

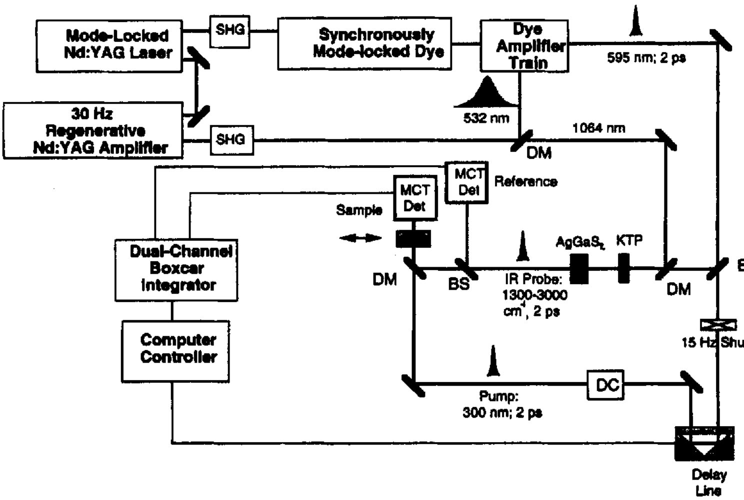


FIGURE 3 Schematic picosecond time-resolved infrared apparatus utilized at Los Alamos (BS = beam splitter; DM = dichroic mirror; MCT = mercury cadmium telluride; SHG = second harmonic generator; DC = doubling crystal). The apparatus is based on a pump-probe technique with time resolution obtained by optically delaying (0.3 mm = 1 ps) an infrared probe pulse with respect to a near UV pump pulse. The pump pulse is obtained by amplifying the output of a dual-jet dye laser (R6G/DODCI) synchronously pumped by a frequency-doubled CW mode-locked Nd: YAG laser (Coherent Antares 76S). Amplification is effected in a three-stage Kiton Red dye amplifier, with a Schott filter acting as a saturable absorber between stages 1 and 2. The amplifier is longitudinally pumped by a frequency-doubled Nd: YAG regenerative amplifier (Continuum RA30, 20 mJ at 532 nm, 60-ps pulses at 30 Hz), seeded by the CW-mode locked Nd: YAG laser. Stages 1 and 2 receive approximately 1 mJ/pulse, and stage 3 receives 10 mJ/pulse of 532-nm pump energy, resulting in ca. 2-ps pulses at 595 nm of up to 0.5 mJ/pulse at 30 Hz repetition rate. The 595 nm pulses are frequency doubled to achieve a pump near 300-nm. The infrared probe pulse is generated in a two-step nonlinear mixing process. In the first step, the difference frequency between 1064 nm (1 mJ) pulses from the regenerative amplifier and the amplified dye pulse (ca. 10%) is generated in a potassium titanyl phosphate (KTP) crystal (3 mm thick) cut at 65 degrees relative to the optical axis for type II phase matching. This generates a near infrared pulse at approximately 1.3 μm. The mid-infrared probe pulse (1.7 ps, FWHM ca. 8 cm^{-1}, 100 nJ) is generated in a second step by differencing the residual 1064-nm pulse with the 1.3 μm pulse in a silver thiogallate ($AgGaS_2$) crystal (3 mm thick) cut at 46 degrees for type II phase matching. The infrared frequency is changed by tuning the dye laser with a two-plate birefringent filter to change the difference frequency.

plexes.[6] Enhancement of the Raman signals is observed when the excitation laser pulse is in resonance with an electronic transition of the excited species. Differences between ground- and excited-state vibrational frequencies provide a basis for inferring structural changes induced by differences in electron density. An excellent example is given by the study of heteroleptic polypyridyl complexes.[7] In terms of supramolecular photochemistry, these complexes represent important building blocks that may allow for the occurrence of photoinduced vectorial intercomponent processes such as energy and electron transfer. To adequately utilize these complexes in different synthetic strategies, the site of excited electron following photolysis must be elucidated.

In the binuclear complex $Ru^{II}(dmp)_2$-(Mebpy-CH_2-CH_2-Mebpy)-$Rh^{III}(dmb)^{5+}$ (dmp is 4,7-dimethyl-1-10-phenanthroline; Mebpy is 4-methyl-2,2′-bipyridine, and dmb is 4,4′-dimethyl-2-2′-bipyridine), selective excitation of the ruthenium chromophore is followed by electron transfer quenching, leading to a charge-separated state containing Ru^{III}-Rh^{II} centers.[8] In this case, the thermally equilibrated ^{3}MLCT excited state involved in the electron transfer process could be either Ru → dmp or Ru → Mebpy-CH_2. Given the similarity between the two ligands, their relative energies are difficult to predict. For the same reason, electronic spectroscopy cannot elucidate information regarding the localization of the excited electron. This information, however, can be obtained from time-resolved resonance Raman spectroscopy using model mononuclear complexes.[8] The TR^3 spectra of $[Ru^{II}(dmp)_3]^{2+}$ and $[Ru^{II}(dmb)_3]^{2+}$ contain characteristic vibrational features of the Ru → dmp (e.g. bands at 1415 and 1303 cm^{-1}) and Ru → dmb (e.g. intense bands at 1210, 1291, 1333, 1449, and 1568 cm^{-1}) MLCT excited states. The TR^3 spectrum of the mixed-ligand complex $Ru^{II}(dmp)_2$-(Mebpy-CH_2-CH_2-Mebpy) shows features belonging to both ^{3}MLCT states, and is essentially coincident with the TR^3 spectrum of a solution containing $[Ru^{II}(dmp)_3]^{2+}$ and $[Ru^{II}(dmb)_3]^{2+}$ in a 2:1 ratio. These results clearly point to an interligand equilibration on the time scale of the experiment (<20 ns) with the excited electron residing with a statistical population (33%) on the bpy-type ligand. This further suggests that the efficient pathway for the electron transfer process would involve the π^* orbital of the Mebpy-CH_2 moiety.

When a more pronounced electronic asymmetry among the coordinated ligands of $[Ru^{II}(LL)(LL')(LL'')]^{2+}$ exists, TR^3 spectra clearly reveal a lowest excited state that has the electron localized on one of the three ligands. Figure 4 shows an example in which the transient Raman

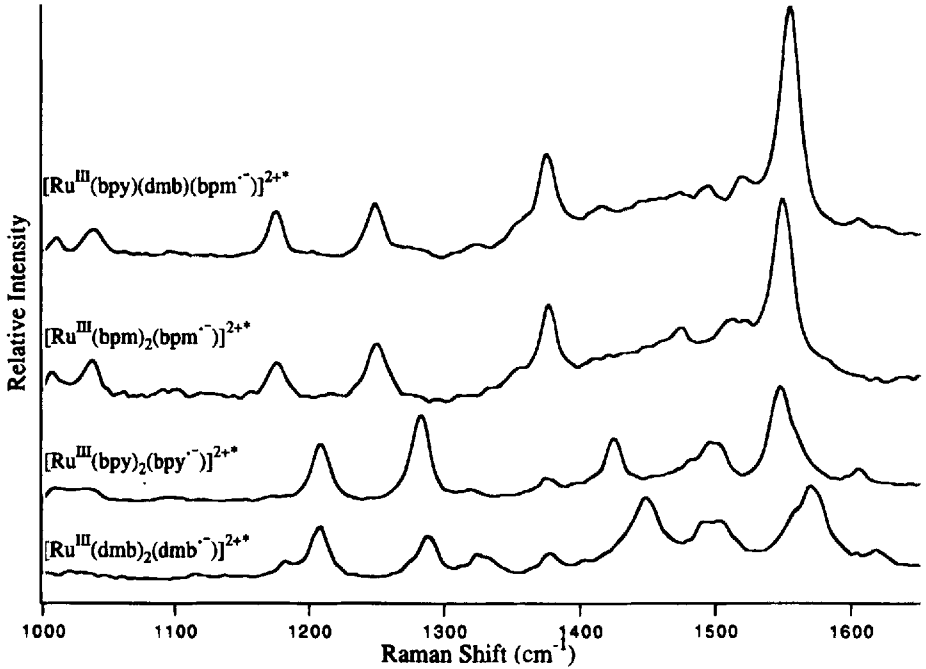


FIGURE 4 Time-resolved resonance Raman spectrum (1000–1650 cm^{-1}) of $[[Ru^{II}(bpy)(dmb)(bpm)]^{2+}$ compared to spectra of $Ru^{II}(bpm)_3]^{2+}$, $[Ru^{II}(bpy)_3]^{2+}$ and $[Ru^{II}(dmb)_3]^{2+}$. The annotation next to the spectrum indicates the assignment of the excited state. Measurements were made in CH_3CN at room temperature using 354.7 nm laser pulses to excited the sample and as a source for the Raman scattering.

spectrum of the MLCT state of [[$Ru^{II}(bpy)(dmb)(bpm)]^{2+}$ is compared to that of $[Ru^{II}(bpy)_3]^{2+}$, $[Ru^{II}(dmb)_3]^{2+}$, and $[Ru^{II}(bpm)_3]^{2+}$ (bpy is 2,2′-bipyridine and bpm is 2,2′-bipyrimidine).[9]

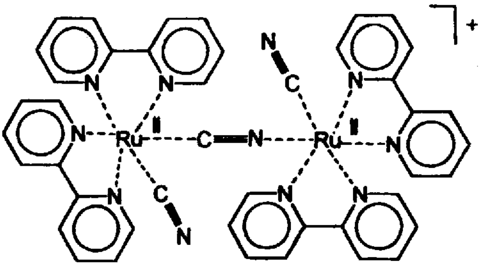
The data were collected on 1 mM samples in degassed CH_3CN with the third harmonic of a pulsed Nd: YAG laser (354.7 nm, 7 ns). The same laser pulse was used to both create the excited state and for a source of the Raman scattering. In the spectrum of $[Ru^{II}(bpy)(dmb)(bpm)]^{2+}$ where bpm has the lowest lying π* acceptor level, Raman bands for $(bpm^{\cdot -})$ (e.g., 1175, 1250, 1520, and 1555 cm^{-1}) dominate the spectrum with only ground-state signals observed originating from the bpy and dmb ligands. No transient bands characteristic of $(bpy^{\cdot -})$ (at 1212, 1284, 1426, 1496, or 1548 cm^{-1}) and $(dmb^{\cdot -})$ (at 1209, 1288, 1324, 1450, 1499, or 1572 cm^{-1}) are observed; thus localization is shown to be on the bpm ligand.

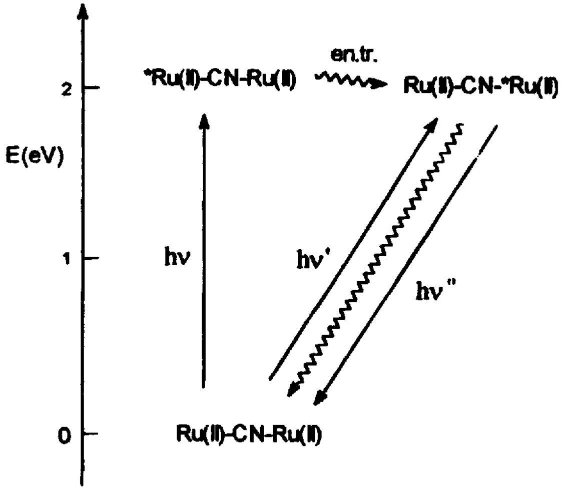
Large ligands and asymmetric ligands in coordination complexes present the possibility of localization of the excited electron within a particular fragment of the ligand. TR^3 spectroscopy is the only experimental technique capable of addressing this issue. Recently, the results of ground- and excited-state Raman measurements have been used to predict the extent of ligand π* framework involvement in the excited state of different ligands. Examples are provided by studies of the excited-state properties of $[Ru(bpy)_2(pypz)]^{2+}$ and $[(dmb)_2Ru^{II}(\mu\text{-bbpe})Ru^{II}(dmb)_2]^{4+}$ (pypz is 2-pyridylpyrazine and μ-bbpe is trans-1,2-bis (4-(4′-methyl)-2,2′bipyridyl)ethane). While for the former localization on the pyrazine portion of the pypz ligand was noted,[10] TR^3 spectra of the μ-bbpe dimer indicated delocalization of the excited electron over the entire bbpe ligand.[11]

4. ENERGY TRANSFER IN POLYNUCLEAR COMPLEXES

Supramolecular systems which utilize excited-state energy transfer processes between molecular components present another area where the TR^3 method provides a spectroscopic probe to clarify the occurrence and direction of these processes.

Studies on polynuclear complexes based on cyano-bridged $Ru(bpy)_2^{2+}$ units have indicated that, by synthetic control of the linkage, intramolecular energy transfer can be driven between MLCT excited states localized on the C and N bonded units (Scheme I).[12] The bridging cyanides provide a relatively strong electronic coupling between metal centers, thus favoring efficient energy transfer processes.





SCHEME I

We have utilized TR[3] spectroscopy and the complexes $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$ and $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(phen)_2(CN)]^+$ to study energy transfer in these systems.[12d] The exchange of phen for bpy is nearly isomorphous electronically, as demonstrated by the properties of $[Ru^{II}(phen)_2(CN)_2]$ and $[Ru^{II}(bpy)_2(CN)_2]$, and yet the two ligands can be distinguished unambiguously by the Raman technique.

The transient Raman spectra of $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$ and $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(phen)_2(CN)]^+$ (Fig. 5) clearly establish the energy transfer product following MLCT excitation. These results can be compared to the transient spectra of $[Ru^{II}(bpy)_3]^{2+}$ and $[Ru^{II}(phen)_3]^{2+}$

as well as the CW Raman data for (bpy·$^-$) and (phen·$^-$).[3b,3f,13,14] The spectrum of $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$ (Fig. 5A) shows strong bands at 745, 1014, 1212, 1285, 1424, and 1549 cm^{-1}, that are essentially that of (bpy·$^-$), with the only features associated with the phen ligand arising from enhancement of ground-state signals. This result is consistent with the assignment of the lowest excited state on the nanosecond time scale as $[(NC)(phen)_2Ru^{II}(CN)Ru^{III}(bpy\cdot^-)(bpy)(CN)]^+$. This state is reached both by direct excitation and indirectly by energy transfer following Ru^{II} → phen excitation. The transient Raman spectrum of $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(phen)_2(CN)]^+$ (Fig. 5B) verifies this result and is dominated by ground-state ν(bpy) bands which gain enhancement from the ground-state $\pi\pi^*$ absorption near 320 nm. Additionally, transient bands of medium intensity at 1315, 1432, and 1583 cm^{-1} are observed, which can be assigned to (phen·$^-$), consistent with the oxidation state distribution of $[(NC)(bpy)_2Ru^{II}(CN)Ru^{III}(phen\cdot^-)(phen)(CN)]^+$ as the primary component following photoexcitation. This cross-check experiment provides convincing evidence that: (i) the lowest MLCT excited state in these quasi-symmetrical complexes always resides on the N-bonded metal-polypyridine unit; (ii) fast and efficient intercomponent energy transfer from C-bonded to N-bonded MLCT states takes place.

TR^3 results further suggest the possibility that protonation of the terminal cyanide on the N-bonded unit can reverse the energy transfer process. For example, the transient Raman spectrum of a solution where the protonated $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CNH)]^{2+}$ is believed to be the primary component shows a loss in intensity of bands of (bpy·$^-$) with a concomitant appearance of (phen·$^-$) features (Fig. 5C).[15]

The previous examples have shown that the effect of synthetic changes or other perturbations of supramolecular systems can be monitored by observing changes in excited-state Raman bands. In the transient Raman studies of energy transfer processes, information as to the presence and direction of energy transfer in cyano-bridged ruthenium complexes depend upon differences in observed ligand vibrations. With the TRIR technique information can be obtained by monitoring ν(CN), which directly probes the metal oxidation state. For $[(NC)(bpy)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$, the transient infrared spectrum following MLCT excitation demonstrates a depletion of the ground-state cyanide bands and the concomitant appearance of new excited-state absorption features.[12c] Comparison of the transient infrared spectrum with that of the chemically produced mixed-valence dimer,

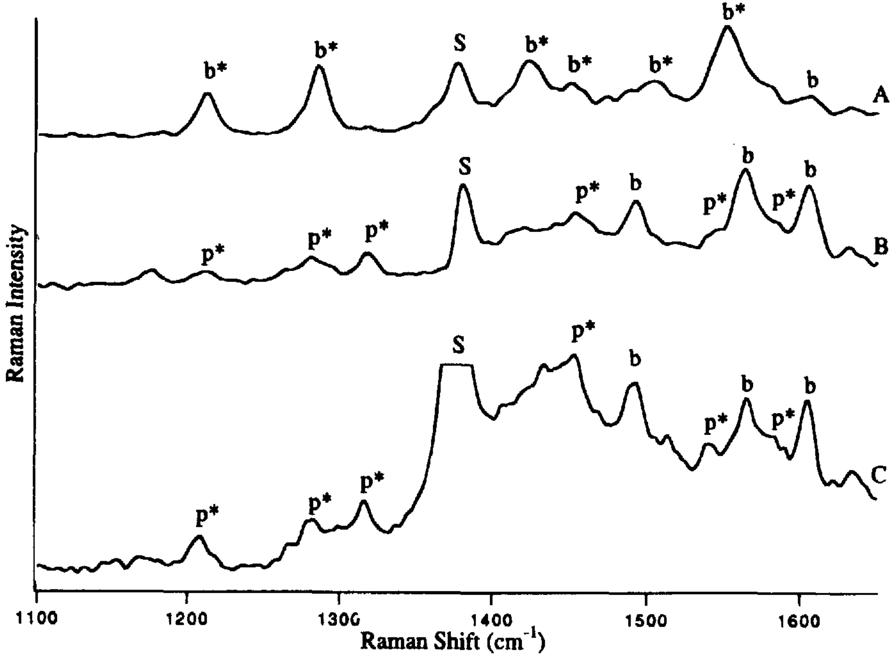


FIGURE 5 Time-resolved resonance Raman spectra (1100–1650 cm^{-1}) of acetonitrile solutions of $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CN)]^+$ (A), $[(NC)(bpy)_2Ru^{II}(phen)_2(phen)_2(CN)]^+$ (B) and $[(NC)(phen)_2Ru^{II}(CN)Ru^{II}(bpy)_2(CNH)]^{2+}$ (C). Measurements were made at room temperature using 354.7 nm laser pulses to excited the sample and as a source for the Raman scattering. Major Raman bands are denoted by p* (excited state phen), b* (excited-state bpy), p (ground-state phen), b (ground state bpy), and S for acetonitrile.

$[(NC)(bpy)_2Ru^{II}(CN)Ru^{III}(bpy)_2(CN)]^{2+}$, allows us to assign the new absorption bands to the stretching modes of the bridging and terminal cyanides, demonstrating that the excited state can be described as $[(NC)(bpy)_2Ru^{II}(CN)Ru^{III}(bpy^{\cdot -})(bpy)(CN)]^{+*}$.[12c]

Polynuclear systems which undergo long-range energy transfer following absorption of a photon can be synthesized. As an example the cyano-bridging chemistry has been extended to the oligomers $[(phen)(CO)_3Re^{I}(CN)[Ru^{II}(bpy)_2(CN)]_n Ru^{II}(bpy)_2]^{(n+1)+}$ in which every Ru^{II} center is linked to two cyanides, one binding to carbon and one to nitrogen. Photophysical studies have suggested that these complexes can function as molecular conduits for long-range energy transfer.[16] The comparison of the transient Raman spectra of the trinuclear $[(phen)(CO)_3 Re^{I}(NC)Ru^{II}(phen)_2(CN)Ru^{II}(bpy)_2(CN)]^{2+}$ and of the model binuclear complexes $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(bpy)_2(CN)]^{+}$ and $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(phen)_2(CN)]^{+}$ provide direct evidence for this long-range transfer.[16] As shown in Fig. 6, simultaneous $Re^{I} \rightarrow$ phen and $Ru^{II} \rightarrow$ bpy excitation in the binuclear complex $[(phen)(CO)_3 Re^{I}(NC)Ru^{II}(bpy)_2(CN)]^{+}$ results in characteristic Raman bands for $(bpy^{\cdot -})$ (Fig. 6A), indicating efficient energy transfer from the Re to the Ru center. Under identical experimental conditions, excitation of $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(phen)_2 (CN)]^{+}$ results in bands attributed to $(phen^{\cdot -})$ (Fig. 6B). For the trinuclear complex $[(phen)(CO)_3Re^{I}(NC)Ru^{II}(phen)_2(CN)Ru^{II}(bpy)_2(CN)]^{2+}$ (Fig. 6C), only bands for $(bpy^{\cdot -})$ appear consistent with complete energy transfer to the terminus within the laser pulse (<10 ns).

5. INTRAMOLECULAR ELECTRON TRANSFER

The study of light-induced electron transfer in electron donor-acceptor systems has typically utilized transient absorption and emission measurements.[17] The Raman technique offers a probe for intramolecular electron transfer processes with more detail and the ability to establish changes in geometry at the acceptor ligand.[18] Differences between ground- and excited-state vibrational frequencies provide a basis for inferring structural and conformational changes induced by differences in electron content.

An interesting example is given by the chromophore-quencher complex *fac*-$[(bpy)Re^{I}(CO)_3(MQ^{+})]^{2+}$, where the N-methyl-4,4′-bipyridinium cation (monoquat or MQ^{+}) is the acceptor ligand. Following

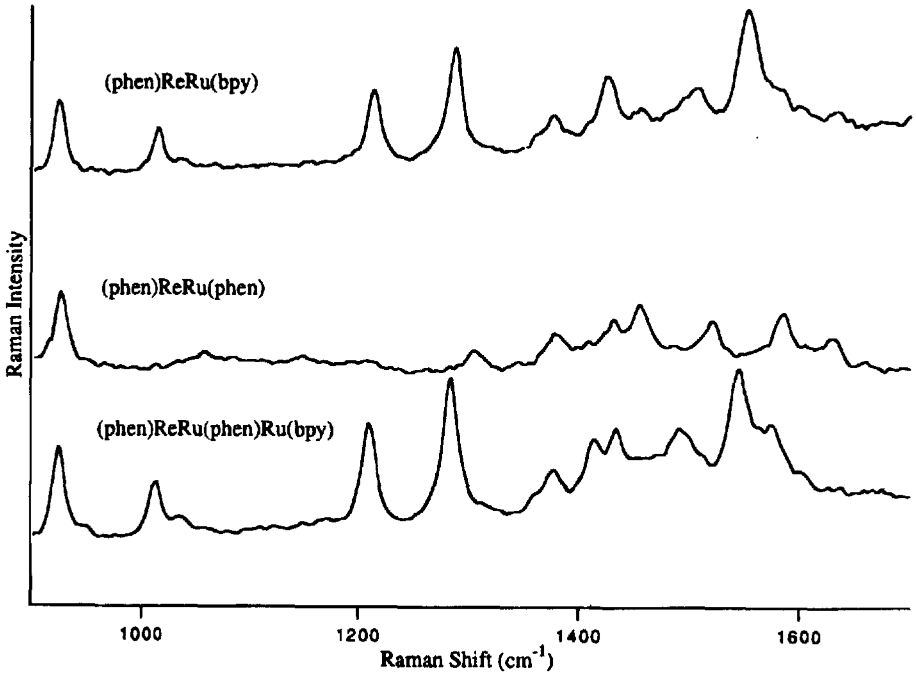


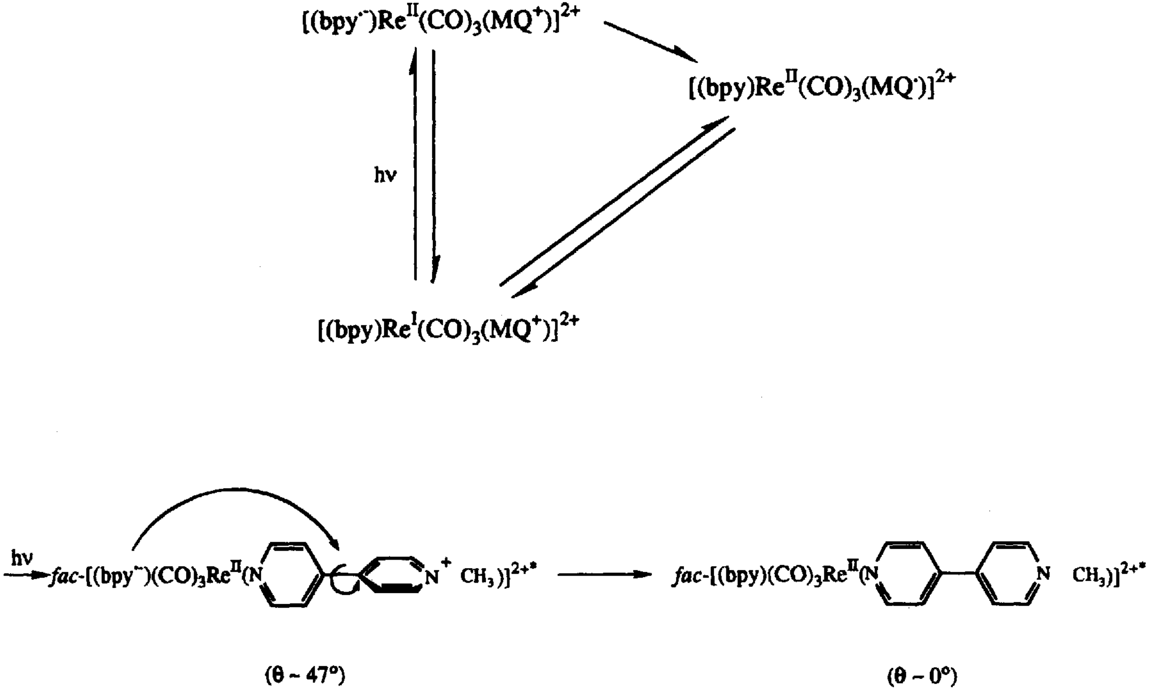
FIGURE 6 Time resolved resonance Raman spectra (900–1650 cm^{-1}) of [(phen)(CO)$_3$Re^I(NC)Ru^{II}(bpy)$_2$(CN)]$^+$ (Top), [(phen)(CO)$_3$Re^I(NC)Ru^{II}(phen)$_2$(CN)]$^+$ (Middle) and [(phen)(CO)$_3$Re^I(NC)Ru^{II}(phen)$_2$(CN)Ru^{II}(bpy)$_2$(CN)]$^{2+}$ (Bottom) in CH$_3$CN. Measurement were made at room temperature using 354.7-nm laser pulses to excited the sample and as a source for the Raman scattering.

$Re^I(d\pi) \rightarrow bpy(\pi^*)$ excitation, intramolecular electron transfer ($bpy^{\cdot -} \rightarrow MQ^+$) occurs to give the lower energy, $Re^{II}(MQ\cdot)$-based MLCT excited state (Scheme II).[17a]

The transient resonance Raman spectra (1000–1700 cm^{-1}) of *fac*-$[Re^I(bpy)(CO)_3(4\text{-}Etpy)]^+$ and *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ are shown in Fig. 7. The band energies for MQ· were established independently by measurements on solutions containing the electrochemically generated, one-electron-reduced complex *fac*-$[Re^I(bpy)(CO)_3(MQ\cdot)]^+$. The occurrence of intramolecular electron transfer following Re→ bpy excitation of fac-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ is clear when the transient spectra of *fac*-$[Re^I(bpy)(CO)_3(4\text{-}Etpy)]^+$ and *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ are compared. The resonantly enhanced Raman bands for *fac*-$[Re^I(bpy)(CO)_3(4\text{-}Etpy)]^+$ are typical of ($bpy^{\cdot -}$) as found in the excited-state spectra of $[Ru^{II}(bpy)_3]^{2+}$ and the CW spectrum of ($bpy^{\cdot -}$). For *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ only bands originating from (–MQ·) (at 1025, 1043, 1202, 1250, 1359, 1502, 1523, 1609 and 1649 cm^{-1}) are observed in the transient spectrum.

Results of vibrational analyses are available for molecules with structural similarities to MQ such as biphenyl and N N′-dimethyl-4,4′-bipyridinium dication (paraquat or PQ^{2+} or methylriologen) and their one-electron reduced forms.[19,20] With these data it is possible to use the transient Raman results to probe structural changes at monoquat that accompany intramolecular electron transfer. The Raman band with a large contribution from the inter-ring C–C stretch ν(C–C) can be assigned in the spectrum of *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ to the band at 1298 cm^{-1}. Upon one-electron reduction, this band shifts to 1348 cm^{-1}, and is observed at 1359 cm^{-1} in the transient spectrum of *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$ indicating an increase in bond order. These data are consistent with a significant amount of charge transfer to MQ^+ in the monoquat-based, MLCT excited state, and points to a shortening in the inter-ring separation distance, a planar, quinoidal structure with $\theta \sim 0°$, and enhanced aromatic character extending across the two rings. The conclusion regarding planarity and $\theta \sim 0°$ are reinforced by the comparison between PQ^{2+} and 3,3′-Me_2PQ^{2+}, where the methyl groups in the ring prevent the pyridine groups from adopting a coplanar conformation. In the one-electron-reduced $PQ^{\cdot +}$, $\nu(C\text{–}C)_{ir}$ is found at 1356 cm^{-1}, while for 3,3′-$Me_2PQ^{\cdot +}$ $\nu(C\text{–}C)_{ir}$ is observed at 1327 cm^{-1}, consistent with less double-bond character between the rings and a lower degree of coplanarity.

When the CW and transient resonance Raman data are combined, structural changes at the monoquat ligand induced by electron transfer


[(bpy˙⁻)Re^II(CO)_3(MQ^+)]^{2+}
[(bpy)Re^II(CO)_3(MQ˙)]^{2+}
hν
[(bpy)Re^I(CO)_3(MQ^+)]^{2+}
hν
fac-[(bpy˙⁻)(CO)_3Re^II(N
N^+ CH_3)]^{2+*}
fac-[(bpy)(CO)_3Re^II(N
N CH_3)]^{2+*}
(θ ~ 47°)
(θ ~ 0°)

SCHEME II

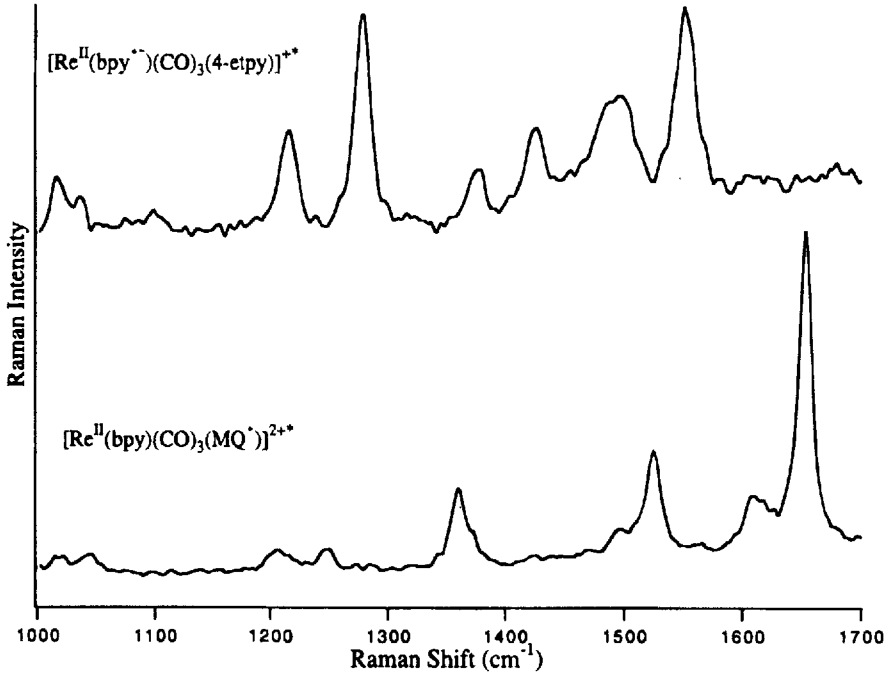


FIGURE 7 Time-resolved resonance Raman spectra (1000–1700 cm^{-1}) of fac-$[Re^{I}(bpy)(CO)_3(4\text{-Etpy})]^+$ and fac-$[Re^{I}(bpy)(CO)_3(MQ^+)]^{2+}$ with the same experimental conditions as used in Fig. 4–6.

can be inferred. For fac$[\mathrm{Re^I(bpy)(CO)_3(MQ^+)}]^{2+}$, from crystallographic data and the frequency of the inter-ring stretch in the CW Raman spectrum, $\theta \sim 47°$.[21] $\mathrm{Re^I} \rightarrow$ bpy excitation followed by bpy $\rightarrow \mathrm{MQ^+}$ electron transfer causes the dihedral angle to decrease to $\theta \sim 0°$ (Scheme II). The conversion between forms implies both a structural change and an associated change in electronic delocalization and resonance energy.[18,21]

6. KINETICS OF INTERCOMPONENT ELECTRON AND ENERGY TRANSFER PROCESSES

The continuing developments in time-resolved resonance Raman and infrared spectroscopy has led to the possibility of investigating very fast intercomponent electron transfer processes. The ability of the $\mathrm{TR^3}$ technique for documenting selective populations of various ligand-localized excited states can allow time resolution of the kinetics of electron transfer processes by monitoring the rise time or decay of specific vibrational transitions. A clear example is given by the study of intraligand electron transfer in mixed-ligand ruthenium (II) complexes containing 2,2′-bipyridine and 2,2′-bipyrimidine (bpm), or 2,2′-bipyridine and 4,4′carboxy-2,2′-bipyridine ($\mathrm{dcbH_2}$).[22] Although the energy gaps between the higher energy ligand (bpy) and the lower energy (bpm) and ($\mathrm{dcbH_2}$) are rather modest (ca. 3100 $\mathrm{cm^{-1}}$), intraligand electron transfer was found complete on a 30 ps or faster time scale.[22]

The presence of suitable ligands giving rise to vibrations with high oscillator strength allow the use of picosecond infrared spectroscopy to estimate the time scale of intercomponent electron or energy transfer processes. This technique has recently been used to investigate electron transfer and vibrational relaxation in cyano-bridged mixed-valence complexes of the type $[\mathrm{(NC)_5M^{II}\text{-}CN\text{-}M^{III}(NH_3)_5}]^-$ (M = Ru, Os),[23] and successfully applied to the study of intramolecular energy transfer in $[\mathrm{(phen)(CO)_3Re^I(NC)Ru^{II}(bpy)_2(CN)}]^+$[24]

Due to the presence of the carbonyl groups on Re, which give rise to very intense infrared stretching bands, the binuclear $[\mathrm{(phen)(CO)_3 Re^I(NC)Ru^{II}(bpy)_2(CN)}]^+$ complex is particularly well-suited for TRIR studies. Because of varying degrees of π-backbonding, different CO stretching frequencies are expected for the ground state, the Re-based MLCT excited state, and the Ru-based MLCT excited state. In the infrared spectrum of the ground state in $\mathrm{CH_3CN}$ (Fig. 8C), ν(CO) bands appear at 1920 and 2028 $\mathrm{cm^{-1}}$, the terminal ν(CN) stretch at 2079 $\mathrm{cm^{-1}}$, and ν(CN) for the bridge at 2094 cm^{-1}. In the nanosecond TRIR spectrum of this system (Fig. 8D), obtained by exciting at 354.7 nm, bleaching of the ground state CO and CN stretching bands are observed, with the rise of new CO and CN excited state bands. The terminal ν(CN) shifts from 2079 to 2108 cm^{-1} with the bridging ν(CN) shifting from 2094 to 2132 cm^{-1}. The shifts in ν(CO) are much smaller ($\Delta\nu(CO) \sim 5$ cm^{-1}) compared to the large shifts observed for the Re → phen, MLCT excited state of the model *fac*-$[Re(phen)(CO_3)(4\text{-}Me\text{-}py)]^+$ (4-Me-py is 4 methylpyridine) (Fig. 8A, 8B). These observations are consistent with energy transfer from the Re-based chromophore, producing the Ru-based MLCT state:

$$*[(CO)_3Re^{I}(phen)\text{–}NC\text{–}Ru^{III}(bpy)(bpy^{-})\text{–}CN]^+$$

The fact that in the dimer the CO ligands on Re still experience a small, but non-negligible, frequency shift is clearly due to the second-sphere effect of Ru transmitted to Re through the bridging cyanide. An estimate of the time scale of the intercomponent transfer process has been obtained by picosecond TRIR.

The 1-ps difference spectrum of this complex (Fig. 9) obtained by exciting at 300 nm (where substantial initial Re → phen excitation is produced) shows spectral features which are very similar to those observed in the nanosecond spectrum of *fac*-$[Re(phen)(CO_3)(4\text{-}Me\text{-}py)]^+$ (Fig. 8B). This is consistent with formation of Re^{II}(phen) in the dimer at the very early times. By monitoring the relaxation of the CO stretching frequencies after excitation, the energy transfer process can be time-resolved, yielding a rate constant of ca. 2×10^{11} s^{-1} for conversion of the Re-based MLCT state into the Ru-based MLCT state.[24]

7. CONCLUSIONS

A number of applications of time-resolved vibrational spectroscopy to the study of excited states of transition metal complexes have been discussed. It has been shown, in particular, that these techniques provide data capable of addressing the problem of excited-state localization and excited-state structure of supramolecular species. The development of ultrafast vibrational spectroscopies offers the opportunity of characterizing the vibrational structure of electronically excited intermediates and to gain insight into the time scale of intercomponent energy and electron transfer processes.

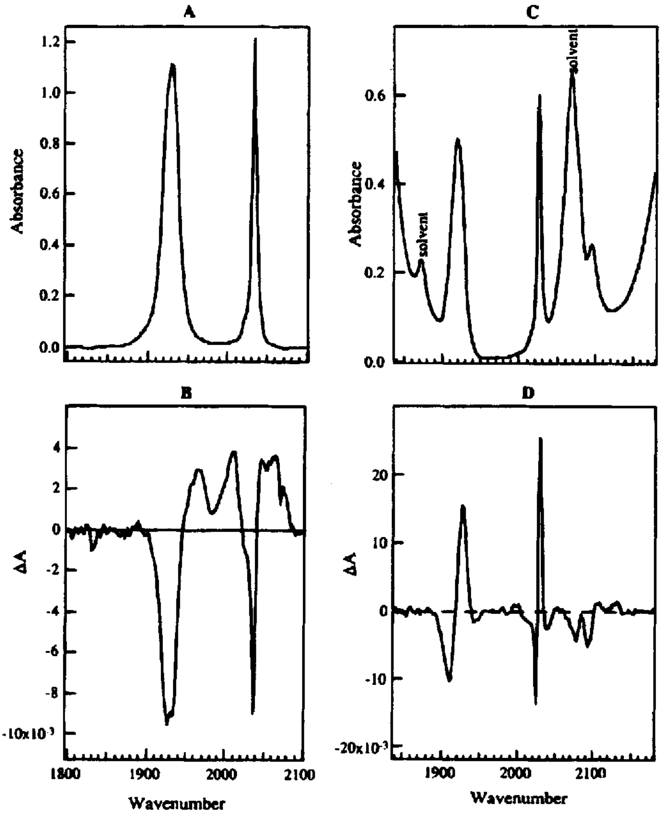


FIGURE 8 Infrared spectra of *fac*-[Re^I(phen)(CO)$_3$(4-Mepy)]$^+$ (A) and [(phen)(CO)$_3$Re^I(NC)Ru^{II}(bpy)$_2$(CN)]$^+$ (C), and 600-ns transient infrared difference spectra of *fac*-[Re^I(phen)(CO)$_3$(4-Mepy)]$^+$ (B) and [(phen)(CO)$_3$Re^I(NC)Ru^{II}(bpy)$_2$(CN)]$^+$ (D) in CH$_3$CN (solvent bands are labelled).

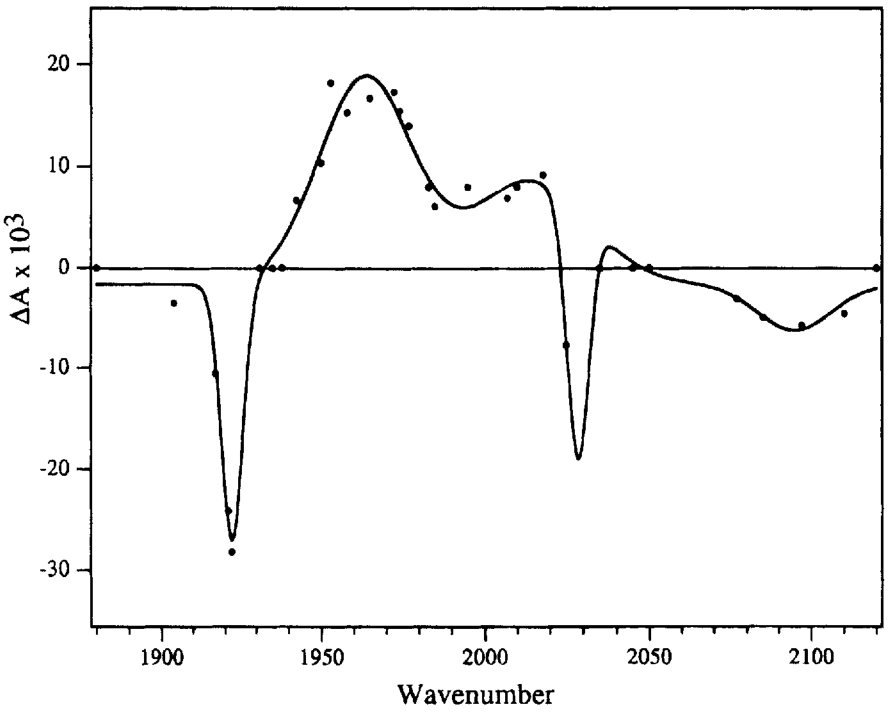


FIGURE 9 Transient infrared difference spectrum of $[(\mathrm{phen})(\mathrm{CO})_3\mathrm{Re}^{\mathrm{I}}(\mathrm{NC})\mathrm{Ru}^{\mathrm{II}}(\mathrm{bpy})_2(\mathrm{CN})]^+$ in CH_3CN, 1 ps after excitation at 300 nm.

References

1. V. Balzani and F. Scandola, *Supramolecular Photochemistry* (Horwood, Chichester, 1991).
2. (a) D. E. Morris and W. H. Woodruff, in *Spectroscopy of Inorganic-Based Materials*, R. J. H. Clark, R. E. Hester (John Wiley & Sons, New York, 1987). (b) C. V. Kumar, J. K. Barton, N. J. Turro and I. R. Gould, Inorg. Chem. **26**, 1455 (1987). (c) D. S. Caswell and T. G. Spiro, Inorg. Chem. **26**, 18 (1987). (d) C. V. Kumar, J. K. Barton, I. R. Gould, N. J. Turro and J. V. Houten, Inorg. Chem. **27**, 648 (1988). (e) T. Yabe, D. R. Anderson, L. K. Orman, Y. S. Chang and J. B. Hopkins, J. Phys. Chem. **93**, 2302 (1989). (f) Y. S. Chang, X. Xu, T. Yave, S. C. You, D. R. Anderson, L. K. Orman and J. B. Hopkins, J. Phys. Chem. **94**, 729 (1990). (g) G. D. Danzer and J. R. Kincaid, J. Phys. Chem. **94**, 3976 (1990). (h) C. Turro, S. H. Bossmann, G. E. Leroi, J. K. Barton and N. J. Turro, Inorg. Chem. **33**, 1344 (1994). (i) S. M. Treffert-Ziemelis, J Golus, D. P. Strommen and J. R. Kincaid, Inorg. Chem. **32**, 3890 (1993). (j) K. C. Gordon and J. J. McGarvey, Inorg. Chem. **30**, 2986 (1991). (k) K. C. Gordon and J. J. McGarvey, Chem. Phys. Lett. **173**, 443 (1990). (l) D. P. Strommen, P. K. Mallick, G. D. Danzer, R. S. Lumpkin and J. R. Kincaid. J. Phys. Chem. **94**, 1357 (1990). (m) G. D. Danzer, J. A. Golus and J. R. Kincaid, J. Am. Chem. Soc. **115**, 8643 (1993).
3. (a) J. J. Turner, M. W. George, F. P. A. Johnson and J. R. Westwell, Coord. Chem. Rev. **125**, 101 (1993). (b) P. O. Stoutland, R. B. Dyer and W. H. Woodruff, Science **257**, 1913 (1992). (c) R. M. Hochstrasser, P. A. Anfinrud, R. Diller, C. Han, M. Iannone, T. Lian and B. Locke, in Ultrafast Phenomena **VII**, 229 (1990). (d) R. A. Palmer, Spectroscopy 8, 26 (1993).
4. (a) R. A. Palmer, C. J. Manning, J. A. Rzepiela, J. M. Widder and J. L. Chao, Appl. Spectrosc. **43**, 193 (1989). (b) R. A. Palmer, J. L. Chao, R. M. Dittmar, V. G. Gregoriou, and S. E. Plunkett, Appl. Spectrosc. **47**, 1297 (1993). (c) W. Uhmann, A. Becker, C. Taran and F. Siebert, Appl. Spectrosc. **45**, 390 (1991). (d) O. Weidlich and F. Siebert, Appl. Spectrosc. **47**, 1394 (1993).
5. J. N. Moore, P. A. Hansen and R. M. Hochstrasser, Chem. Phys. Lett. **138**, 110 (1987)
6. (a) J. McClanahan, R. F. Dallinger, F. J. Holler and J. R. Kincaid, J. Am. Chem. Soc. **107**, 4853 (1985). (b) P. A. Mabrouk and M. S. Wrighton, Inorg. Chem. **25**, 526 (1986).
7. G. F. Strouse, P. A. Anderson, J. R. Schoonover, T. J. Meyer and F. R. Keene, Inorg. Chem. **31**, 3004 (1993).
8. M. T. Indelli, C. A. Bignozzi, A. Harriman, J. R. Schoonover and F. Scandola, J. Am. Chem. Soc. **116**, 3768 (1994).
9. S. L. Mecklenberg, D. G. McCafferty, J. R. Schoonover, B. M. Peek, B. W. Erickson and T. J. Meyer, Inorg. Chem. **33**, 2974 (1994).
10. G. D. Danzer, J. A. Golus and J. R. Kincaid J. Am. Chem. Soc. **115**, 8643 (1993).
11. G. F. Strouse, J. R. Schoonover, R. Duessing, S. Boyde, W. E. Jones and T. J. Meyer, Inorg. Chem. **34**, 473 (1995).
12. (a) C. A. Bignozzi, S. Roffia, C. Chiorboli, J. Davila, M. T. Indelli and F. Scandola, Inorg. Chem. **28**, 4350 (1989). (b) F. Scandola, M. T. Indelli, C. Chiorboli and C. A. Bignozzi, Topics Curr. Chem. **73**, 158 (1990). (c) C. A. Bignozzi, R. Argazzi, K. C. Gordon, R. B. Dyer, J. R. Schoonover and F. Scandola, Inorg. Chem. **31**, 5260 (1992). (d) C. A. Bignozzi, R. Argazzi, C. Chiorboli, F. Scandola, R. B. Dyer, J. R. Schoonover and T. J. Meyer, Inorg. Chem. **33**, 1652 (1994).
13. (a) R. F. Dallinger and W. H. Woodruff, J. Am. Chem. Soc. **101**, 4391 (1979). (b) P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger and W. H. J. Woodruff, J. Am. Chem. Soc. **103**, 7441 (1981). (c) W. K. Smothers and M. S. Wrighton, J. Am. Chem. Soc. **105**, 1067 (1983). (d) P. K. Mallick, D. P. Strommen and J. R. Kincaid, J. Am.

Chem. Soc. **112**, 1686 (1990). (e) P. K. Mallick, G. D. Danzer, D. P. Strommen and J. R. Kincaid, J. Phys. Chem. **92**, 5628 (1988).

14. (a) J. R. Schoonover, unpublished results. (b) M. A. Malueg, Dissertation, The University of Texas, Austin, 1981.
15. C. A. Bignozzi, J. Davila, J. R. Schoonover and F. Scandola, manuscript in preparation.
16. C. A. Bignozzi, R. Argazzi, C. G. Garcia, F. Scandola, J. R. Schoonover and T. J. Meyer, J. Am. Chem. Soc. **114**, 8727 (1992).
17. (a) P. Chen, E. Danielson and T. J. Meyer, J. Phys. Chem. **92**, 3708 (1988). (b) T. D. Westmoreland, H. LeBozec, R. W. Murray and T. J. Meyer, J. Am. Chem. Soc. **105**, 5952 (1983). (c) P. Chen, T. D. Westmoreland, E. Danielson, K. S. Schanze, D. Anthon, P. E. Neveux and T. J. Meyer, Inorg. Chem. **26**, 1116 (1987). (d) P. Chen, R. Duesing, G. Tapolsky and T. J. Meyer, J. Am. Chem. Soc. **111**, 8305 (1989). (e) K. S. Schanze and K. Sauer, J. Am. Chem. Soc. **110**, 1180 (1988). (f) D. B. MacQueen and K. S. Schanze, J. Am. Chem. Soc. **113**, 7470 (1991). (g) L. S. Fox, M. Kozik, J. R. Winkler and H. B. Gray, Science, **247**, 1069 (1990). (h) S. L. Carson, L. F. Cooley, C. M. Elliot and D. F. Kelley, J. Am. Chem. Soc. **114**, 9504 (1992). (i) T. J. Meyer, in *Photochemical Processes in Organized Molecular Systems, ed.* N. Kitamura (Elsevier, Amsterdam, 1991), p. 133.
18. J. R. Schoonover, P. Chen, W. D. Bates and T. J. Meyer, Inorg. Chem. **33**, 793 (1994).
19. C. Takahashi and S. Maeda, Chem. Phys. Lett. **24**, 585 (1974).
20. R. E. Hester and K. P. Williams, J. Chem. Soc. Perkin Trans. **2**, 852 (1981).
21. P. Chen, M. Curry and T. J. Meyer, Inorg. Chem. **28**, 2271 (1989).
22. T. Yabe, L. K. Orman, D. R. Andeison, S. C. Yu, X. Xu and J. B. Hopkins, J. Phys. Chem. **94**, 7128 (1990).
23. S. K. Doom, R. B. Dyer, P. O. Stoutland and W. H. Woodruff, J. Am. Chem. Soc. **115**, 6389 (1993).
24. J. R. Schoonover, K. C. Gordon, R. Argazzi, K. A. Peterson, C. A. Bignozzi, R. B. Dyer and T. J. Meyer, J. Am. Chem. Soc. **115**, 10996 (1993).