Inorg. Chem. **1996,** *35,* 273−274

Application of Time-Resolved, Step-Scan Fourier Transform Infrared Spectroscopy to Excited-State Electronic Structure in Polypyridyl Complexes of Rhenium(I)

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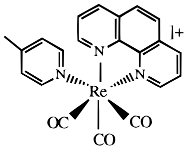
Received July 14, 1995

Recent advances in transient infrared spectroscopy have provided the means for infrared measurements to be made following laser excitation on short time scales.[1] The infrared technique is particularly valuable in the study of metal complexes containing CO or CN^- because ν(CO) and ν(CN) stretching vibrations have high oscillator strengths and the sensitivities of their energies and bandwidths to electronic and molecular structure are well established. Electronic excitation generally produces significant transient infrared absorption changes which are intense and characteristic of the changes in electron structure between states. For example, in $[(phen)(CO)_3Re(NC)Ru(bpy)_2(CN)]^+$ (phen is 1,10-phenanthroline; bpy is 2,2′-bipyridine) $Re^I(d\pi) \rightarrow phen(\pi^*)$ excitation produces initially a $Re^{II}(phen^{\bullet -})$ metal-to-ligand charge transfer (MLCT) excited state and large shifts in ν(CO) (40−80 cm^{-1}) compared to those in the ground state. Subsequently, rapid cross-bridge energy transfer occurs ($k_q \sim 2 \times 10^{11}$ s^{-1}) to give $[(phen)(CO)_3Re^I(NC)Ru^{III}(bpy)(bpy^{\bullet -})(CN)]^{+*}$ which is accompanied by a shift of +57 cm^{-1} in the terminal ν(CN) band and only a slight shift in ν(CO) compared to the ground state.[2] Here we apply step-scan transient infrared to the elucidation of the excited-state electronic structure in complexes **1**−**3**. There is a complicated interplay between MLCT and ligand-based excited states in these complexes.[3] They have found use in the study of nonradiative decay,[4] long-range electron and energy transfer,[5] and the Marcus "inverted" region.[6] We have returned to the question of excited-state electronic structure by employing a powerful new approach to acquiring time-resolved infrared spectroscopy based on the step-scan Fourier transform technique.



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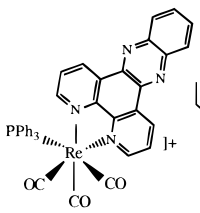

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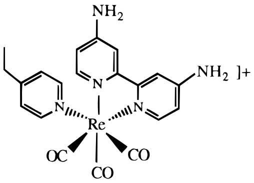

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The ground-state infrared spectrum and transient difference spectrum in the ν(CO) region for *fac*-$[Re(phen)(CO)_3(4\text{-}Mepy)]^+$ (**1**, phen is 1,10-phenanthroline; 4-Mepy is 4-methylpyridine) are shown in Figure 1A. The difference spectrum was acquired 600 ns after 354.7 nm excitation in CH_3CN by using step-scan FTIR.[7] In the spectrum, the ground state ν(CO) band at 1930 cm^{-1} splits and shifts to higher energy with new bands appearing at 1962 and 2009 cm^{-1}.[8] The ground-state band at 2036 cm^{-1} shifts to 2062 cm^{-1}. These shifts are consistent with oxidation of Re(I) to Re(II) and formation of an MLCT excited state.[1a,2,9]

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

The difference spectrum for **2**, *fac*-$[Re(dppz)(CO)_3(PPh_3)]^+$

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(7) The details of the time-resolved step-scan FTIR experiment will be published elsewhere (Schoonover, J. R.; Dyer, R. B. Manuscript in preparation). Briefly, the experiment uses a Q-switched Nd:YAG laser (Spectra Physics GCR-11) as the pump source (7 ns, 200 μJ pulse, 10 Hz) and a BioRad FTS 60A step-scan interferometer as the IR source. The collimated IR beam from the interferometer is tightly focused (ca. 300 μm spot diameter), overlapped with the pump beam in the sample, and then detected with a photovoltaic MCT detector. The signal from the MCT detector is processed in two matched boxcar integrators; one gate is placed before the time zero and the other starting at time zero. The time resolution is determined by the width of the gate (600 ns). The laser repetition rate, interferometer step rate, and boxcar integration are synchronized at 10 Hz. The two integrated signals yield a "dark" and "light" single-beam spectrum, from which the transient difference spectrum is computed as $\Delta A = -\log(\text{“light”}/\text{“dark”})$. Each time-resolved spectrum is an average of 64 scans at 4 cm^{-1} resolution with a free spectral range of 3850 cm^{-1} (2233 steps per scan, one laser shot per step).

(8) The low-energy ν(CO) band in the ground state splits in the excited state as a consequence of reduced symmetry.[2]

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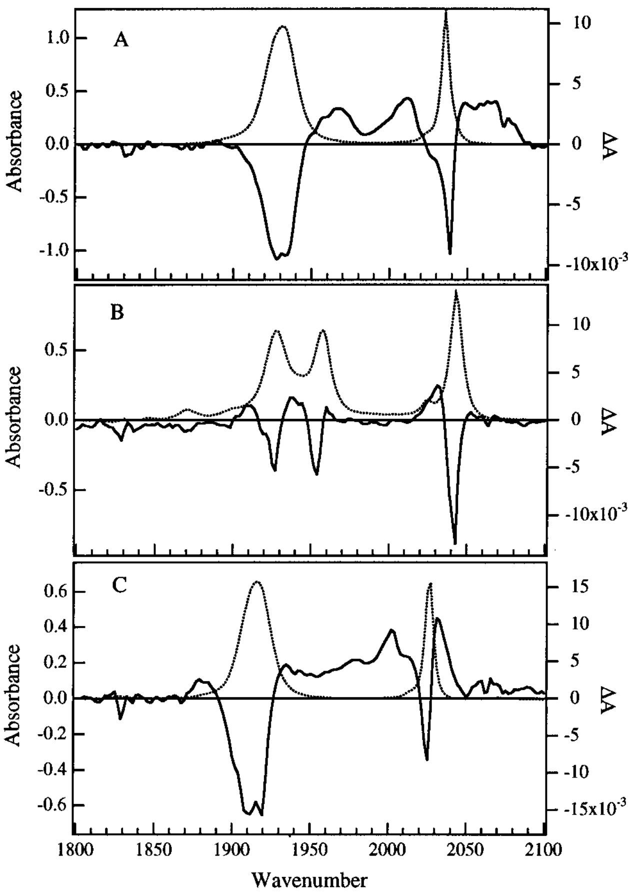

Figure 1. Ground-state (broken curve) and 600 ns time-resolved difference FTIR spectra of (A) *fac*-[Re(phen)(CO)$_3$(4-Mepy)]$^+$ (**1**; phen is 1,10-phenanthroline; 4-Mepy is 4-methylpyridine), (B) *fac*-[Re(dppz)-(CO)$_3$(PPh$_3$)]$^+$ (**2**; dppz is dipyrido[3,2-*a*:2′,2′-*c*]phenazine; PPh$_3$ is triphenylphosphine), and (C) *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) in CH$_3$CN at room temperature 600 ns after 354.7 nm excitation.[7]

(dppz is dipyrido[3,2-*a*:2′,2′-*c*]phenazine; PPh$_3$ is triphenylphosphine), under the same conditions is shown in Figure 1B. In this spectrum, the three ν(CO) bands shift only slighly in the excited state, and significantly, *the shifts are to lower energy*. The transient difference spectrum can be simulated quantitatively by including six Gaussian line shapes (three ground- and three excited-state bands). From the fit, each ν(CO) band in the excited state is shifted on average 8 cm^{-1} to lower energy and broadened by ~2 cm^{-1} compared to those in the ground state.

The relative magnitudes of the shifts in ν(CO) are revealing. The large shifts to higher energy for **1** are expected for an MLCT excited state in which Re(I) is formally oxidized in Re(II). Similar shifts have been observed for the MLCT excited states of [Re(bpy)(CO)$_3$(4-Etpy)]$^+$ (4-Etpy is 4-ethylpyridine) and [Re-(4,4′-bpy)(CO)$_3$Cl] (4,4′-bpy is 4,4′-bipyridine).[1a,2,9] The small shifts for **2** are consistent with a lowest, ligand-localized excited state, presumably $^3\pi\pi^*$(dppz). This interpretation is consistent with room-temperature emission from this complex which has the characteristic, resolved vibronic structure and extended excited-state lifetime ($\tau = 42\ \mu$s) of a $^3\pi\pi^*$ excited state.[10] When PPh$_3$ is replaced by Cl$^-$ in *fac*-[Re(dppz)(CO)$_3$Cl], $^3\pi\pi^*$(dppz) remains lowest lying, but at room temperature excited-state emission and decay are dominated by thermal population and decay from a slightly higher MLCT state.[10] The fact that the shifts in ν(CO) are to lower energy in **2** shows that, in the excited state, Re(I) is a better electron donor to CO than in the ground state. By inference, $^3\pi\pi^*$(dppz) is a better electron donor to Re(I) than ground-state dppz.

The power of the step-scan transient IR technique to elucidate electronic structure is also illustrated by measurements on **3**, *fac*-[Re(4,4′-(NH$_2$)$_2$bpy)(CO)$_3$(4-Etpy)]$^+$ (4,4′-(NH$_2$)$_2$bpy is 4,4′-diamino-2,2′-bipyridine). UV−visible excitation in fluid solution results in appearance of a characteristic MLCT emission with λ_{max} = 570 nm.[11] In transient UV−visible absorption difference spectra, there is evidence for both a ligand-localized excited state (or states), with a broad absorption feature at 450 nm, and an MLCT excited state with a $\pi \rightarrow \pi^*$(4,4′-(NH$_2$)$_2$-bpy$^{\bullet-}$) band appearing at 370 nm. The relative intensities of the two are solvent and temperature dependent.[11]

The transient infrared difference spectrum for **3** in CH$_3$CN is shown in Figure 1C. The features that appear can be attributed to an MLCT excited state and at least one additional, 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 **1**. ν(CO) bands are also observed shifted to lower energy at 1881 and 2014 cm^{-1} which are comparable to the shifts observed for the $^3\pi\pi^*$ state of **2**. There is evidence for still a third set of excited-state bands at 1930 and 2031 cm^{-1} reinforced by simulations, suggesting the possibility of a third excited state probably ligand-centered. These observations are consistent with the results of transient UV−visible absorption which provide evidence for at least two coexisting states in fluid solution.[11] Temperature-dependent transient infrared studies will be required to resolve futher this mixture of excited states.

These results demonstrate the utility of step-scan FTIR in obtaining transient infrared spectra of transition metal complexes. They provide a new dimension by utilizing oxidation-state-sensitive CO stretches to distinguish between excited states of different orbital origins. The technique also addresses questions pertaining to internal electronic structure such as back-bonding and oxidation state based on the magnitudes of ν(CO) shifts. There is a further advantage that the step-scan technique can be applied throughout the infrared region, including bands arising from the polypyridine ligands. We are currently pursuing transient infrared measurements on [Ru(bpy)$_3$]$^{2+}$ and related complexes.

Acknowledgment. This work was performed in part at Los Alamos National Laboratory under the auspices of the U.S. Department of Energy and supported by Laboratory Directed Research and Development Project No. 94292 to J.R.S. Work at UNC was supported by the Department of Energy, Grant DE-FG05-86ER13633 to T.J.M.

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