Inorg. Chem. **1997,** *36,* 954−955

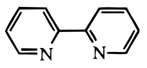
Insights on the Excited State Electronic Structures of Ruthenium(II) Polypyridine Complexes Obtained by Step-Scan Fourier Transform Infrared Absorption Difference Time-Resolved Spectroscopy

Pingyun Chen,[†] Kristin M. Omberg,[‡] Darius A. Kavaliunas,[‡] Joseph A. Treadway,[‡] Richard A. Palmer,*,[†] and Thomas J. Meyer*,[‡]

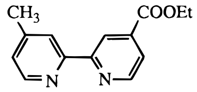
Departments of Chemistry, Duke University, Box 90346, Durham, North Carolina 27708-0346, and University of North Carolina, Chapel Hill, North Carolina 27599-0359

Received November 1, 1996

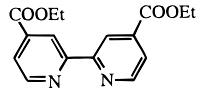
Application of time-resolved infrared spectroscopy has had an important impact on transition metal photochemistry.[1] The emphasis has been on metal carbonyl and metal cyano complexes because the oscillator strengths of $\bar{\nu}$(CO) and $\bar{\nu}$(CN) are high, and tunable lasers are available in the relevant spectral region.[2] Until recently, time-resolved infrared spectroscopy using Fourier transform interferometry has been limited to a time resolution of ≥ 5 μs. However, application of step-scan FT-IR has greatly expanded the time window.[3,4] It is now possible to acquire spectra with high resolution and sensitivity on a time scale of tens of nanoseconds over the entire mid-IR region.[5] In this communication, we report the application of step-scan FT-IR absorbance difference time-resolved spectroscopy (S^{2}FT-IR ΔA TRS) with *spectra acquired on the 10 ns time scale* to the study of electronic structure in the metal-to-ligand charge transfer (MLCT) excited states of two related complexes of ruthenium(II) containing only the ligands 2,2′-bipyridine (bpy), 4-(carboxyethyl)-4′-methyl-2,2′-bipyridine (4-COOEt-4′-CH$_3$bpy) and 4,4′-(dicarboxyethyl)-2,2′-bipyridine (4,4′-(COOEt)$_2$bpy):



(bpy)



(4-COOEt-4′-CH$_3$bpy)



(4,4′-(COOEt)$_2$bpy)

Comparison of the relative vibrational energies of the MLCT states leads to specific and significant conclusions regarding the distribution of electron density in these states.

Spectra were obtained on a step-scan-modified Bruker IFS 88 FT-IR spectrometer. Samples were dissolved in acetonitrile in sufficient concentration (~5 mM) to give an absorbance between 0.2 and 0.6 for the ester C═O stretch at 1731 cm^{-1} in a 0.25 mm path length. The solutions were sparged with argon before loading by syringe into the CaF$_2$-windowed IR cell. For the S^{2}FT-IR ΔA TRS, or ΔA, measurements, samples were excited by third-harmonic pulses (355 nm) from a Quanta Ray DCR-1 Nd:YAG laser (10 ns at 10 Hz; 3 mJ/pulse). The data acquisition sequence was controlled by a Stanford Research Model 455 pulse generator. Data were collected at 2−6 cm^{-1} spectral resolution. The liquid-N$_2$-cooled Kolmar Technologies MCT detector was operated in the AC/DC-coupled mode and had an effective rise time of ~20 ns. Spectra before and after the laser pulse were sampled at 10 ns intervals. The effects of a total of 100−300 laser flashes were averaged for each of the interferogram points. The transient absorption difference spectra ΔA (after-minus-before) were calculated from the single-beam ΔI transforms by the relation $\Delta A(\bar{\nu},t) = -\log[1 + \Delta I(\bar{\nu},t)/I(\bar{\nu})]$, where $I(\bar{\nu})$ is the intensity before laser excitation and $\Delta I(\bar{\nu},t)$ is the change in intensity at time t.

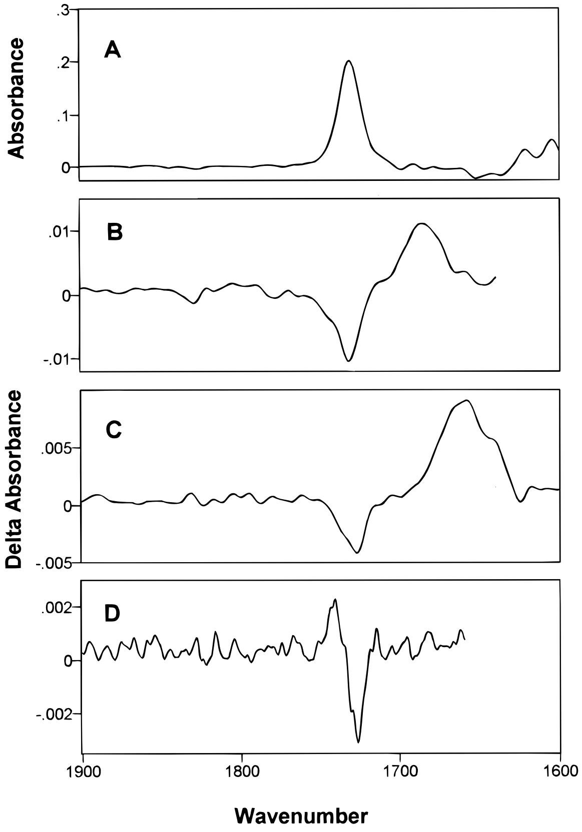


Figure 1. FT-IR spectra in CH$_3$CN: (A) ground state spectrum of [Ru(bpy)$_2$(4-COOEt-4′-CH$_3$bpy)]$^{2+}$; (**1**) (B) laser-induced ΔA spectrum of **1** in the absence of any quencher; (C) ΔA spectrum of **1** in the presence of the reductive quencher 10-methylphenothiazine; (D) ΔA spectrum of **1** in the presence of the oxidative quencher methylviologen. The ΔA spectra are the averages of the first ten 10-ns time slices after the laser pulse.

In Figure 1 are shown (A) the ground state FT-IR spectrum of [Ru$^{\mathrm{II}}$(bpy)$_2$(4-COOEt-4′-CH$_3$bpy)]$^{2+}$ (**1**) and (B−D) its ΔA

[†] Duke University.

[‡] The University of North Carolina.

(1) (a) Bignozzi, C. A.; Argazzi, R.; Chiorboli, C.; Scandola, F.; Dyer, R. B.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 1652. (b) Turner, J. J.; George, M. W.; Johnson, F. P. A.; Westwell, J. R. *Coord. Chem. Rev.* **1993**, *125*, 101. (c) Bignozzi, C. A.; Argazzi, R.; Schoonover, J. R.; Gordon, K. C.; Dyer, R. B.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 5260. (d) Doorn, S. K.; Gordon, K. C.; Dyer, R. B.; Woodruff, W. H. *Inorg. Chem.* **1992**, *31*, 2284.

(2) (a) Schoonover, J. R.; Chen, P.; Bates, W. D.; Dyer, R. B.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 793. (b) Doorn, S. K.; Dyer, R. B.; Stoutland, P. O.; Woodruff, W. H. *J. Am. Chem. Soc.* **1993**, *115*, 6398. (c) Doorn, S. K.; Stoutland, P. O.; Dyer, R. B.; Woodruff, W. H. *J. Am. Chem. Soc.* **1992**, *114*, 3133.

(3) (a) Palmer, R. A. *Spectroscopy* **1993**, *8*, 26. (b) Palmer, R. A.; Chao, J. L.; Dittmar, R. M.; Gregoriou, V. G.; Plunkett, S. E. *Appl. Spectrosc.* **1993**, *47*, 1297.

(4) Schoonover, J. R.; Strouse, G. F.; Dyer, R. B.; Bates, W. D.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 273.

(5) (a) Weidlich, O.; Siebert, F. *Appl. Specrtrosc.* **1993**, *47* 1394. (b) Palmer, R. A.; Chen P. *Microchim. Acta* **1997**, *Suppl. 14*, 595.

S0020-1669(96)01328-6 CCC: $14.00

Table 1. Ester $\bar{\nu}(\mathrm{C{=}O})$ Band Energies and Shifts in $\mathrm{CH_3CN}$ at Room Temperature

complex[b]	$\bar{\nu}$ ($\mathrm{cm^{-1}}$)	$\Delta\bar{\nu}$ ($\mathrm{cm^{-1}}$)[a]	Figure 1 spectrum
$[\mathrm{Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)}]^{2+}$ (**1**)	1731		A
$[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{2+}*$ (**2**)	1685	−46	B
$[\mathrm{Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{+}$ (**3**)	1660	−71	C
$[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)}]^{3+}$ (**4**)	1741	$+{<}10$	D
$[\mathrm{Ru^{II}(bpy)_2(4,4'\text{-}(COOEt)_2bpy)}]^{2+}$ (**5**)	1731		
$[\mathrm{Ru^{III}(bpy)_2(4,4'\text{-}(COOEt)_2bpy^{\bullet-})}]^{2+}*$ (**6**)	1705	−26	
$[\mathrm{Ru^{II}(bpy)_2(4,4'\text{-}(COOEt)_2bpy^{\bullet-})}]^{+}$ (**7**)	1688	−43	

[a] $\bar{\nu}$(after) − $\bar{\nu}$(before) the laser pulse. [b] As $\mathrm{PF_6^-}$ salts.

spectra (generated as described above) in the absence of any quencher, in the presence of the reductive quencher 10-methylphenothiazine (10-MePTZ), and in the presence of the oxidative quencher methylviologen (*N*,*N*′-dimethyl-4,4′-bipyridinediium dication, $\mathrm{MV^{2+}}$). The reductive and oxidative quenching reactions give $[\mathrm{Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{+}$ (**3**) and $[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)}]^{3+}$ (**4**), respectively, by eqs 1 and 2. The absorption band at 1731 $\mathrm{cm^{-1}}$ in Figure 1A is $\bar{\nu}(\mathrm{C{=}O})$ of the ester group in the ground state (**1**), and the positive bands in difference spectra in Figure 1B−D give the energies of this vibration in $[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{2+}*$(**2**), $[\mathrm{Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{+}$(**3**), and $[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)}]^{3+}$(**4**), respectively. The spectrum of the symmetrically substituted (diester) analog $[\mathrm{Ru^{II}(bpy)_2(4,4'\text{-}(COOEt)_2bpy)}]^{2+}$ (**5**) and the corresponding ΔA spectra for $[\mathrm{Ru^{III}(bpy)_2(4,4'\text{-}(COOEt)_2bpy^{\bullet-})}]^{2+}*$(**6**) and $[\mathrm{Ru^{II}(bpy)_2(4,4'\text{-}(COOEt)_2bpy^{\bullet-})}]^{+}$ (**7**) were obtained under the same conditions. The results of both sets of experiments are summarized in Table 1.

$$\underset{\mathbf{2}}{[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{2+}*} + \text{10-MePTZ} \rightarrow \underset{\mathbf{3}}{[\mathrm{Ru^{II}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{+}} + \text{10-MePTZ}^{+} \tag{1}$$

$$\underset{\mathbf{2}}{[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy^{\bullet-})}]^{2+}*} + \mathrm{MV^{2+}} \rightarrow \underset{\mathbf{4}}{[\mathrm{Ru^{III}(bpy)_2(4\text{-}COOEt\text{-}4'\text{-}CH_3bpy)}]^{3+}} + \mathrm{MV^{\bullet+}} \tag{2}$$

There are several important features in these data that pertain to excited state electronic structure:

(1) There is a small (<10 $\mathrm{cm^{-1}}$) positive shift in the energy of the ester $\bar{\nu}(\mathrm{C{=}O})$ band for the monoester complex between $\mathrm{Ru^{II}}$ and $\mathrm{Ru^{III}}$ (**1** and **4**). This is due to loss of $d\pi(\mathrm{Ru})-\pi^*$(4-COOEt-4′-$\mathrm{CH_3}$bpy) back-bonding to the ester group upon oxidation.

(2) The large negative shifts in $\bar{\nu}(\mathrm{C{=}O})$ of the ester group in the MLCT excited states (**2** and **6**) reveal that the excited electron is localized on the ester-bearing ligand in these mixed chelates and that the ester group is highly mixed into the lowest π^* acceptor level.

(3) The appearance of a single ester $\bar{\nu}(\mathrm{C{=}O})$ band for the MLCT excited state of the diester complex (**6**), with a shift about half that for the monoester complex (**2**), demonstrates that *the excited electron is delocalized over both pyridine rings in the diester ligand.* It is delocalized in the mixed-valence sense, at least on the infared time scale.

(4) The larger shift for the monoester-based excited state (**2**) is consistent with a high degree of polarization toward the ester-substituted pyridine in the lowest π^* acceptor level. This observation complements the transient resonance Raman results obtained by Kincaid and co-workers on asymmetrically substituted bipyridine derivatives.[6]

(5) The magnitudes of the excited state shifts of the ester $\bar{\nu}(\mathrm{C{=}O})$ frequency in the MLCT excited states (**2** and **6**) are about two-thirds those for the corresponding fully reduced complexes (**3** and **7**). This demonstrates that polarization effects are important in these excited states, with considerable $d\pi(\mathrm{Ru^{III}})$ mixing with the π^* acceptor orbital.

Our data show that $\mathrm{S^2}$FT-IR ΔA TRS can be applied meaningfully to the study of short-lived excited states and intermediates and that measurements on ligand vibrations (other than those of classic “reporter” CO and $\mathrm{CN^-}$ ligands) can provide useful insights into electronic distribution in these excited states.

Acknowledgments are made to the Department of Energy for Grant 5-35972 to T.J.M. and to the National Science Foundation for Grant 9409107 to R.A.P.

IC961328P

---

(6) (a) Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643. (b) Treffert-Ziemelis, S. M.; Golus, J. A.; Strommen, D. P.; Kincaid, J. R. *Inorg. Chem.* **1993**, *32*, 3890.