

Interpretation of the Time-Resolved Resonance Raman Spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$

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Introduction

The initial, and subsequent, time-resolved resonance Raman (TR^3) spectra of the metal-to-ligand charge transfer (MLCT) excited state(s)¹ of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy is 2,2'-bipyridine)^{2,3} showed that localization of the excited electron and $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^{2+*}$ is a better description than delocalization and $[\text{Ru}(\text{bpy}^{1/3\bullet-})_3]^{2+*}$, at least on the nanosecond time scale.⁴ This conclusion was verified by transient infrared difference spectra by observing bpy bands in the mid-IR fingerprint region (1400–1700 cm^{-1}).⁵

It was reported recently that excited-state phen bands are not observed in the TR^3 spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$, and this was claimed as evidence for delocalization in the lowest MLCT excited state(s) of this complex.⁶ If this is true, there is a striking and profound difference in excited-state properties between $[\text{Ru}$

(bpy)₃]²⁺ and $[\text{Ru}(\text{phen})_3]^{2+}$, which are otherwise closely related in their electronic and molecular structures. An alternate interpretation of the TR^3 spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ is presented here which favors localization in its lowest MLCT state(s) as well.

Experimental Section

Sample Preparation. $[\text{Li}^+(\text{phen}^{\bullet-})]$, ~2 mM in tetrahydrofuran (distilled from LiAlH_4 and then potassium metal), was prepared by reduction of anhydrous 1,10-phenanthroline with an excess of lithium metal under an inert atmosphere. Extreme caution was used to keep the reagents and reaction vessel oxygen- and water-free. The initially colorless solution turned deep blue as the reaction progressed. The blue solution was transferred under an inert atmosphere to an absorbance/Raman cell of our own design. The absorption spectrum of the ion-paired anion exhibited bands at 394 nm ($\epsilon \sim 10,000 \text{ L mol}^{-1} \text{ cm}^{-1}$), 582 nm ($\epsilon \sim 3,000 \text{ L mol}^{-1} \text{ cm}^{-1}$), and 631 nm ($\epsilon \sim 3,000 \text{ L mol}^{-1} \text{ cm}^{-1}$) with a shoulder at 538 nm. The solutions were highly oxygen- and water-sensitive and at >2 mM side reactions occurred as evidenced by the production of violet or brown solutions.

$[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$ was prepared by bulk electrolysis of 2 mM $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ at -1.44 V vs SSCE in acetonitrile-*d*₃ containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate and transferred to sealed Raman and UV-visible absorption cells under nitrogen. The initially orange solution turned dark brown-red as the reduction progressed. The absorption spectrum of the reduced form exhibited multiple absorptions in the UV and visible including an intense absorption feature at 393 nm.

Raman Measurements. Resonance Raman (RR) spectra were acquired as previously described by using continuous wave excitation at 350.7, 406.7, or 457.9 nm.⁷ Time-resolved resonance Raman (TR^3) spectra were measured by using the third harmonic (354.7 nm) of a Quanta-Ray DCR-2A pulsed Nd:YAG laser both to create the excited state and as a source for the Raman scattering. The scattered radiation was collected in a 135° backscattering geometry into a SPEX 1877 Triplemate spectrometer equipped with 1800 grooves/mm grating. Optimum laser power for the experiment was determined by monitoring the sample emission while adjusting the laser power. When emission intensity no longer increased with laser power, it was assumed that irradiance saturation was achieved (laser power was typically between 3 and 5 mJ/pulse depending upon focusing conditions). The Raman signal was detected by a Princeton Instruments IRY-700G optical multichannel analyzer operating in the gated mode with a ST-110 OSMA detector controller. Timing was controlled by a Princeton Instruments FG-100 pulse generator. Data collection and storage were controlled by an IBM AT with Princeton Instruments SMA software. Samples of $[\text{Ru}(\text{phen})_3](\text{PF}_6)_2$ for TR^3 measurements, ~3 mM in acetonitrile, were deoxygenated by at least three cycles of freeze-pump-thaw degassing.

Results

In the absorption spectra of $[\text{Li}^+(\text{phen}^{\bullet-})]$, $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$, and $[\text{Ru}(\text{phen})_3]^{2+*}$, intense $\pi \rightarrow \pi^*$ absorptions are observed which are based on the partly or fully reduced ligand, including a band that appears at 394 nm in all three spectra. This band is significantly red-shifted compared to $\pi \rightarrow \pi^*$ for $\text{bpy}^{\bullet-}$ in $[\text{Ru}(\text{bpy})_3]^{2+*}$ which appears at 370 nm. Ground-state Raman band energies from the RR spectrum of $[\text{Ru}(\text{phen})_3]^{2+}$ measured with 350.7-nm excitation in water are listed in Table 1. They are compared with TR^3 data for $[\text{Ru}(\text{phen})_3]^{2+*}$ (354.7 nm pulse and probe in acetonitrile, ~4 mJ per pulse) and RR

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- (4) Typical ns TR^3 experiments on $[\text{Ru}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ utilize a single laser pulse (354.7 nm) both to excite the sample and as the source for resonance Raman scattering from a $\pi \rightarrow \pi^*$ transition localized largely on the partially reduced polypyridyl acceptor ligand. The Raman signal is integrated over the period of the gate used in the detection system (ca. 400 ns) which is centered on the laser pulse. Given this arrangement, a precise time resolution is not defined, but, in practical terms, excited states must have lifetimes of 50 ns or longer, depending on the sensitivity of the detector system. The resulting "spectrum" is an average over the time range of the gate. For $[\text{Ru}(\text{bpy})_3]^{2+}$ under conditions of irradiance saturation (~4 mJ per pulse), where the emission intensity no longer increases with laser power, ground-state-like bpy bands persist in the spectrum. They originate from near-resonance enhancement of $\pi \rightarrow \pi^*$ absorptions in the nonacceptor bpy ligands in $[\text{Ru}^{\text{III}}(\text{bpy})_2(\text{bpy}^{\bullet-})]^{2+*}$ which appear at higher energy.
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Table 1. Raman Band Energies (in cm^{-1}); Bands in All Three Spectra Are Indicated in Boldface Type

| $[\text{Ru}(\text{phen})_3]^{2+ a,b}$ | $[\text{Li}^+(\text{phen}^{\bullet-})]^{a,c}$ | $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^{+ d}$ | $[\text{Ru}(\text{phen}^{\bullet-})(\text{phen})_2]^{2+* e}$ | origin |
|---------------------------------------|---|--|--|---------------------------|
| 1115 w | | | | phen |
| | 1119 m | 1120 | 1130 | phen^{•-} |
| 1148 w | | 1150 | 1150 | phen |
| 1209 w | 1212 m | 1205 | 1208 | phen + phen ^{•-} |
| 1255 w | | | | phen |
| | 1254 m | 1252 | 1272 | phen^{•-} |
| 1301 w | | 1287 | | phen |
| 1312 m | 1281 m | 1308 | 1306 | phen + phen ^{•-} |
| | 1335 m | 1341 | | phen ^{•-} |
| | 1421 m | | | phen ^{•-} |
| 1433 m | | 1432 | 1433 | phen |
| 1454 m | 1453 m | 1450 | 1455 | phen + phen ^{•-} |
| 1516 w | 1515 m | 1510 | 1516 | phen + phen ^{•-} |
| | 1543 m | 1546 | | phen ^{•-} |
| 1582 m | | 1577 | | phen |
| | 1587 w | 1591 | 1585 | phen^{•-} |
| 1604 w | | 1605 | 1605 | phen |
| 1634 m | | 1632 | 1632 | phen |

^a Relative Intensities are indicated as follows: m = medium; w = weak. ^b In water, 293 K, 350.7 nm excitation. ^c In tetrahydrofuran, 293 K, 406.7 nm excitation. ^d In acetonitrile- d_3 , 293 K, 406.7 nm excitation. Solvent appears at 1376 and $\sim 1450 \text{ cm}^{-1}$. ^e In acetonitrile, 293 K, 354.7 nm pulsed excitation. Solvent appears at 1376 and $\sim 1450 \text{ cm}^{-1}$.

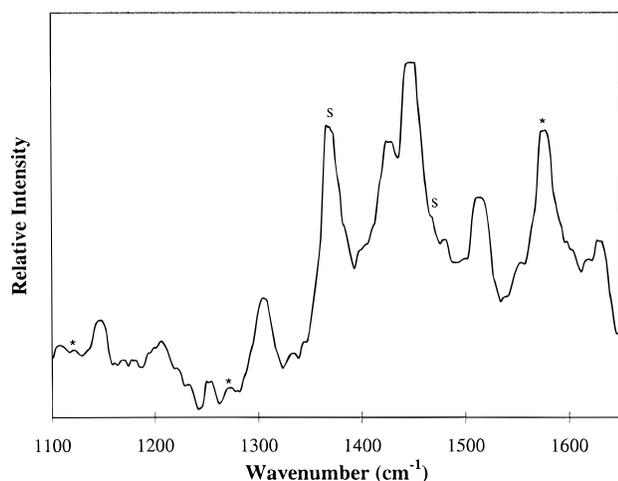


Figure 1. TR^3 spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ (354.7 nm excitation and scattering, $\sim 4 \text{ mJ}$ per pulse), $\sim 3 \text{ mM}$ in acetonitrile at 298 K. Bands from $\text{phen}^{\bullet-}$ are labeled with “*”. Solvent bands appear at 1376 and $\sim 1450 \text{ cm}^{-1}$ and are labeled “S”.

data for $[\text{Li}^+(\text{phen}^{\bullet-})]$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$ (406.7 nm excitation in acetonitrile). There is a reasonable correlation between resonantly enhanced bands for $[\text{Li}^+(\text{phen}^{\bullet-})]$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$. The phen radical anion is a very weak Raman scatterer even with excitation relatively close to the intense $\pi \rightarrow \pi^*$ band at 394 nm.

The TR^3 spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ from 1100 to 1650 cm^{-1} , shown in Figure 1, includes ground-state Raman bands even at high laser irradiances. Comparison between the RR spectra of $[\text{Li}^+(\text{phen}^{\bullet-})]$ and $[\text{Ru}^{\text{II}}(\text{phen}^{\bullet-})(\text{phen})_2]^+$ in Figure 2 show that many of the $\text{phen}^{\bullet-}$ bands are near in energy to ground-state bands (Table 1). There is no overlap between ground-state and transient RR bands at 1130, 1272, and 1585 cm^{-1} . These bands are labeled with “*” in Figures 1 and 2 and shown in boldface type in Table 1. Bands of low intensity are observed near 1270 and 1580 cm^{-1} in the TR^3 spectrum of $[\text{Os}(\text{phen})(\text{py})_4]^{2+}$ as well, and related observations have been made on other phen complexes.⁸ By using a difference approach to obtain TR^3 spectra, Hopkins et al. suggested that RR bands for $[\text{Ru}(\text{phen})_3]^{2+*}$ appear at 1130, 1208, 1272, 1306, 1455, 1516, and 1585 cm^{-1} .³

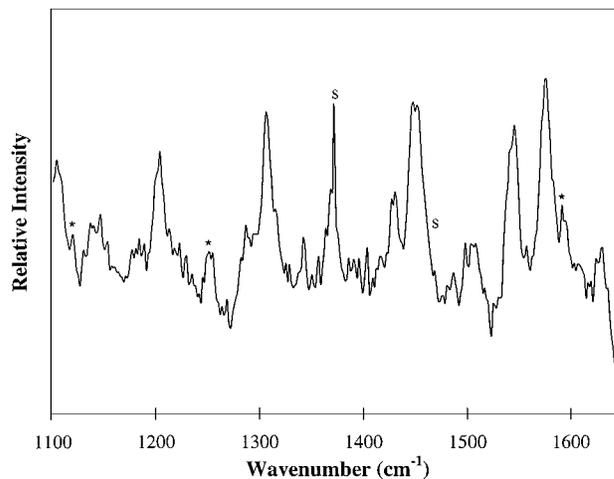


Figure 2. RR of spectrum $[\text{Ru}(\text{phen}^{\bullet-})(\text{phen})_2]^+$ (406.7 nm excitation), $\sim 3 \text{ mM}$ in acetonitrile- d_3 at 298 K. Bands from $\text{phen}^{\bullet-}$ are labeled with “*”. Solvent bands appear at 1376 and $\sim 1450 \text{ cm}^{-1}$ and are labeled “S”.

Discussion

In contrast to an earlier report, the data presented here provide evidence for distinct $\text{phen}^{\bullet-}$ bands in the TR^3 spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ at 1130, 1272, and 1585 cm^{-1} . In the TR^3 spectrum of $[\text{Ru}(\text{bpy})_3]^{2+*}$, there is considerable resonance enhancement because the $\text{bpy}^{\bullet-} \pi \rightarrow \pi^*$ absorption at 370 nm is near the excitation line at 354.7 nm. The $\text{phen}^{\bullet-} \pi \rightarrow \pi^*$ absorption for $[\text{Ru}(\text{phen})_3]^{2+*}$ occurs at 394 nm, which greatly decreases the resonance effect.

In addition, resonance Raman intensities are intrinsically lower for phen than for bpy. They scale as the square of the dimensionless displacement between states, Δ_j , which is related to the electron-vibrational coupling constant, S_j , by, $S_j = 1/2(\Delta_j)^2$. Application of a Franck–Condon analysis and the single mode approximation to emission from a series of $\text{Os}^{\text{II}}(\text{bpy})$ and $\text{Os}^{\text{II}}(\text{phen})$ complexes showed that S is systematically lower by up to $\sim 20\%$ for phen compared to bpy as acceptor ligand at the same energy gap.⁹ In this case, the S values are the sum of S_j 's for a series of coupled ring stretching modes from 1100 to 1650 cm^{-1} . The difference between the S values is due to the greater rigidity of phen compared to bpy.^{7a} Application of a

Franck–Condon analysis to emission from $[\text{Ru}(\text{phen})_3]^{2+*}$ and $[\text{Ru}(\text{bpy})_3]^{2+*}$ in acetonitrile at room temperature gave $S = 0.93$ (phen) and 1.13 (bpy).^{9a,10} This decrease in S and associated changes in equilibrium displacement decrease the resonance effect. The greater rigidity of the phen ligand also decreases the difference in band energies between the ground and MLCT excited state.

Interpretation of the TR^3 spectrum of $[\text{Ru}(\text{phen})_3]^{2+*}$ based solely on the spectrum of “ $\text{Li}^+(\text{phen}^-)$ ” can also be misleading. This method of generating the anion uses a large excess of

lithium which may produce the doubly reduced anion with a distinct spectrum of its own.^{6b} Electrochemical generation of $[\text{Ru}^{\text{II}}(\text{phen}^-(\text{phen})_2)]^+$ by controlled-potential electrolysis circumvents this problem and agreement between our data for $[\text{Ru}^{\text{II}}(\text{phen}^-(\text{phen})_2)]^+$ and $[\text{Ru}(\text{phen})_3]^{2+*}$ points to the presence of partly reduced phen in $[\text{Ru}(\text{phen})_3]^{2+*}$.

On the basis of these data, we conclude that $[\text{Ru}(\text{phen})_3]^{2+*}$ is best described as $[\text{Ru}^{\text{III}}(\text{phen}^-(\text{phen})_2)]^{+*}$, at least on the $\sim\text{ns}$ time scale of the TR^3 experiment. This is consistent with the localized description advanced earlier for $[\text{Ru}(\text{bpy})_3]^{2+*0.2,5}$

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