Communications

Assignment of Electronic Transitions in Mixed-Valence Complexes by Resonance Raman Spectroscopy

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The intensity in the resonance Raman effect is derived from underlying electronic transitions with enhancements occurring for bands for which there is a change in equilibrium displacement between the ground and excited states for corresponding normal modes. The technique has been applied to the elucidation of molecular vibrations in coordination compounds,[1] and recently, Doorn and Hupp have applied it to mixed-valence complexes to analyze vibrational barriers to intramolecular electron transfer.[2,3] We present here in preliminary form an application of the technique to $[(bpy)_2ClOs(CN)Ru(NH_3)_5]^{3+/2+}$ (bpy = 2,2'-bipyridine) which illustrates its power in assigning electronic transitions in spectra where there are overlapping absorption bands. Our observations reinforce those of Doorn and Hupp[2,3] and provide supporting evidence for a proposed "remote" metal-to-ligand charge-transfer (MLCT) transition in $[(bpy)_2ClOs^{II}$-$(CN)Ru^{II}(NH_3)_5]^{2+}$.[4,5]

The syntheses and characterization of $[(bpy)_2ClOs^{II}(CN)$-$Ru^{III}(NH_3)_5]^{3+}$, $[(bpy)_2(CN)Os^{II}(CN)Ru^{III}(NH_3)_5]^{3+}$, and the dibridged complex $[(bpy)_2Os^{II}((CN)Ru^{III}(NH_3)_5)_2]^{6+}$ as PF_6^- salts followed from those for the analogous complexes of ruthenium.[4] They were isolated as mixed-valence salts with the Os^{II}–Ru^{II} forms generated in solution by the addition of hydrazine. From cyclic voltammetric measurements on $[(bpy)_2ClOs^{II}$-$(CN)Ru^{III}(NH_3)_5](PF_6)_3$ in H_2O, 0.1 M in $[N(Et)_4][Cl]$, $E_{1/2}(Ru^{III/II}) = -0.24$ V and $E_{1/2}(Os^{III/II}) = 0.42$ V vs SCE. The UV–visible spectra of the [2,2] and [2,3] forms of this complex are shown in Figure 1. The spectrum of [2,3] consists of a series of overlapping bands at 360, 438, and 558 nm and in the near-infrared at 810 and 1168 nm in addition to the characteristic $\pi \rightarrow \pi^*$ bands below 300 nm.

Wavelength-dependent Raman measurements provide a straightforward method for assigning these transitions. In Figure 2 are shown representative Raman spectra for $[(bpy)_2ClOs^{II}$-$(CN)Ru^{III}(NH_3)_5]^{3+}$ in H_2O with laser excitation at 476.2 and 647.1 nm along with the spectrum of $[(bpy)_2ClOs^{II}(CN)Ru^{II}$-$(NH_3)_5]^{2+}$ with excitation at 520.8 nm. As for the mixed-valence ions studied by Doorn and Hupp,[2] low-energy excitation (647.1,
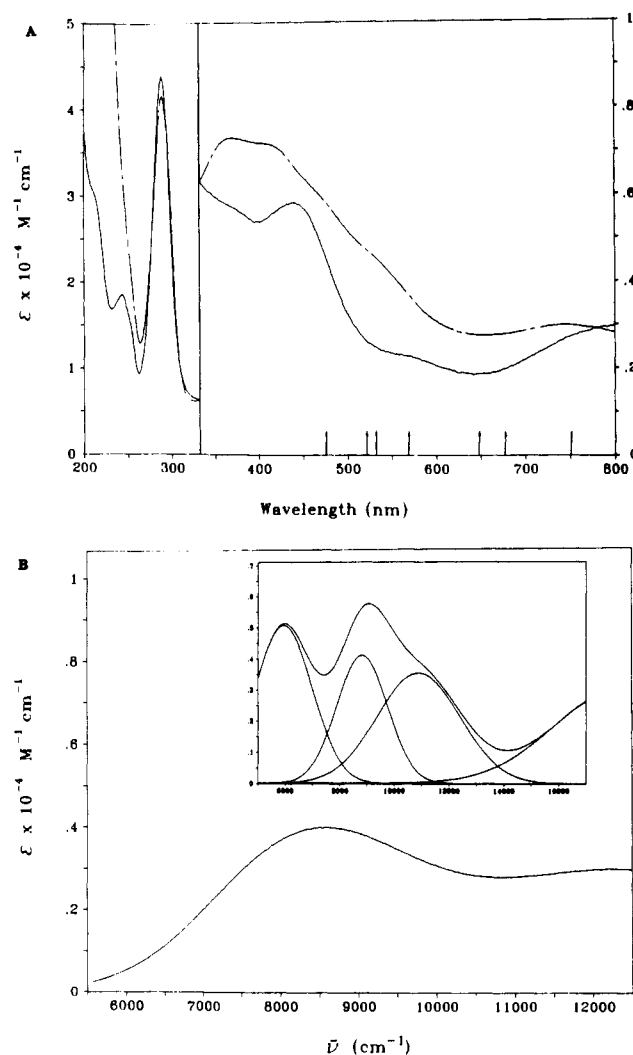
Figure 1. (A) UV–visible spectra of $[(bpy)_2ClOs^{II}(CN)Ru^{III}(NH_3)_5]^{3+}$ (solid trace) and $[(bpy)_2ClOs^{II}(CN)Ru^{II}(NH_3)_5]^{2+}$ in H_2O (broken trace). The laser excitation wavelengths utilized in the Raman experiments are indicated with arrows. (B) Near-infrared absorption spectrum of $[(bpy)_2ClOs^{II}(CN)Ru^{III}(NH_3)_5]^{3+}$ in D_2O. The inset demonstrates the three resolved IT bands observed in nitrobenzene solution. Spectra were recorded on a Cary 14 spectrophotometer modified by On-Line Instruments.

676.4, and 752.5 nm) leads to enhancement of Raman bands associated with low-wavenumber skeletal modes and of $\nu(CN)$ of the bridging cyanide at 1993 cm^{-1}. The enhanced bands include $\delta(H_3N–Ru–NH_3)$ at 238, $\nu(Os–Cl)$ at 282 cm^{-1}, $\nu(Ru–NC)$ at 370 cm^{-1}, $\nu(Ru–NH_3)$ at 470 and 483 cm^{-1}, and $\nu(Os–C)$ at 609

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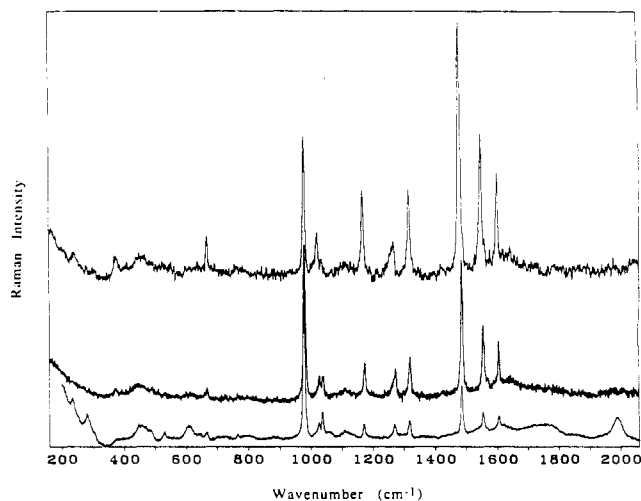
Figure 2. Resonance Raman spectra of $[(bpy)_2ClOs^{II}(CN)Ru^{III}(NH_3)_5]^{3+}$ in H_2O (0.5 M in Na_2SO_4) with laser excitation at 647.1 nm (bottom spectrum) and 476.2 nm (middle spectrum) and $[(bpy)_2ClOs^{II}(CN)-Ru^{II}(NH_3)_5]^{2+}$ obtained with excitation at 520.8 nm (top spectrum). The spectra were normalized in frequency and intensity to the 981-cm^{-1} peak of $SO_4{}^{2-}$. The laser source was a Coherent INNOVA 90K Kr^+ laser. The scattered radiation was dispersed by a Jobin Yvon U1000 double monochromator and detected by a Hamamatsu R943-02 cooled photomultiplier tube with signal processing by an Instruments SA Spectra Link photon-counting system. The spectra are the average of 16 accumulations. The spectral resolution is 4 cm^{-1}.

cm^{-1}.[2,6] This result is consistent with the assignment of the band at 810 nm as an intervalence-transfer (IT) transition ($Os^{II} \rightarrow Ru^{III}$) in a localized mixed-valence complex. On the basis of the solvent dependence of this absorption band and of the longer wavelength band at 1168 nm, the latter can be assigned to an IT transition as well. In nitrobenzene all three of the expected IT bands are observed (at 918, 1133, and 1681 nm; inset Figure 1), which is the first time this has been observed experimentally.[7]

Excitation at 647.1 nm also enhances the bipyridine bands at 376, 669, 767, 1028, 1040, 1109, 1175, 1274, 1371, 1489, 1557,

and 1609 cm^{-1}, but the origin of the enhancement appears to lie in the absorption band at 558 nm. With shorter wavelength excitation (568.2, 530.9, 520.8, 476.2 nm) their intensities are enhanced, while the bands associated with the low-wavenumber skeletal modes and $\nu(CN)$ decrease. No enhancement of the bands attributed to skeletal modes was observed upon excitation at 520.8 or 476.2 nm. The excitation wavelength dependence for $[(bpy)_2(CN)Os^{II}(CN)Ru^{III}(NH_3)_5]^{3+}$ and $[(bpy)_2Os^{II}((CN)-Ru^{III}(NH_3)_5)_2]^{6+}$ are similar. These results are consistent with the assignment of the bands at 438 and 558 nm to $Os^{II} \rightarrow$ bpy MLCT transitions.

In the UV–visible spectrum of $[(bpy)_2ClOs^{II}(CN)Ru^{II}-(NH_3)_5]^{2+}$ a band appears at 530 nm in H_2O which has been assigned to a remote MLCT transition.[4,5]

$$[(bpy)_2ClOs^{II}(CN)Ru^{II}(NH_3)_5]^{3+} \xrightarrow{h\nu}$$

$$[(bpy)(bpy^{\bullet-})ClOs^{II}(CN)Ru^{III}(NH_3)_5]^{3+}$$
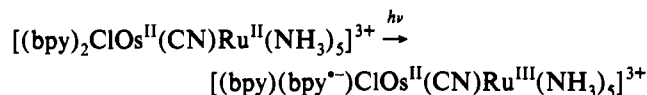
Evidence in support of this assignment can be found in Figure 2. Especially relevant are the enhancements of $\delta(H_3N-Ru-NH_3)$ at 241 cm^{-1} and $\nu(Ru-NH_3)$ near 460 cm^{-1} upon excitation at 520.8 nm.[8] In addition, excitation of [2,2] at 520.8 nm causes enhancement of the bands for the bpy modes by a factor of 2 compared to excitation of [2,3] at either 520.8 or 476.2 nm.[9] This enhancement is expected for a transition associated with a metal to bpy charge transfer.

Our observations support the earlier assignment of the remote MLCT transition and add to the earlier observations of Doorn and Hupp on enhancement of Raman bands in mixed-valence complexes.[3,4] Finally, and most importantly, they provide a clear demonstration of the utility of resonance Raman spectroscopy in assigning electronic transitions in complicated, overlapping absorption spectra.

(6) Resonance Raman spectra in the region near 450 cm^{-1} were complicated by the presence of scattering of the glass sample tube and a vibration due to the sulfate ion which serves as an internal standard. The Raman frequencies in this region were acquired with spectra of samples containing no internal standard and in a low temperature (77 K) cell in which there was no interferences from these two processes.

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(9) (a) The frequencies and intensities in these spectra were referenced to the 981-cm^{-1} Raman peak of sulfate present as 0.5 M Na_2SO_4. (b) This enhancement occurs even though the absorptions of the solution at the excitation wavelengths of 520.8 nm for [2,2] and 476.2 nm for [2,3] are the same.