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Resonance-Enhanced Raman Scattering in the Near-Infrared Region. Preliminary Studies of Charge Transfer in the Symmetric Dimers $(2,2'\text{-bpy})_2\text{ClRu-}4,4'\text{-bpy-RuCl}(2,2'\text{-bpy})_2{}^{4+/3+/2+}$, $(\text{H}_3\text{N})_5\text{Ru-}4,4'\text{-bpy-Ru}(\text{NH}_3)_5{}^{6+/5+/4+}$, and $(\text{NC})_5\text{Fe-}4,4'\text{-bpy-Fe}(\text{CN})_5{}^{4-/5-/6-}$

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Abstract: Three symmetrical mixed-valence dimers (and their oxidized and reduced congeners) have been examined in solution by Raman spectroscopy with use of near-infrared excitation (1064 nm, Nd:YAG source). The specific systems were $(2,2'\text{-bpy})_2\text{ClRu-}4,4'\text{-bpy-RuCl}(2,2'\text{bpy})_2{}^{4+/3+/2+}$, $(\text{H}_3\text{N})_5\text{Ru-}4,4'\text{-bpy-Ru}(\text{NH}_3)_5{}^{6+/5+/4+}$, and $(\text{NC})_5\text{Fe-}4,4'\text{-bpy-Fe}(\text{CN})_5{}^{4-/5-/6-}$. At 1064 nm the excitation source is nearly in resonance with the metal-to-metal or intervalence charge-transfer transition found in each of the mixed-valence ions. Consequently, resonance-enhanced scattering might be expected. From time-dependent Raman scattering theory, this would then provide a basis for a mode-by-mode evaluation of the Franck–Condon factors associated with intervalence charge transfer (*J. Am. Chem. Soc.* **1989**, *111*, 1142). For two of the mixed-valence ions, resonance-enhanced Raman scattering indeed is found. (For the third, the decacyano ion, extensive thermal degradation occurs.) Studies of the corresponding fully reduced ions show, however, that the enhancement effects are due not to intervalence excitation but to weakly preresonant metal-to-ligand excitation. Nevertheless, the experiments do serve to indicate the conditions that will likely be necessary in order to observe intervalence enhancement in symmetrical systems.

One of the more exciting developments in Raman spectroscopy in the last 3–4 years has been the extension of the technique into the near-infrared (near-IR).[1-3] This task is nontrivial because of both the ν^4 attenuation of scattering intensity and the comparative inferiority of near-IR photon detectors. Nevertheless, near-infrared Raman spectroscopy has been demonstrated experimentally by two means: (1) Fourier-transform averaging of the (signal independent) detector-noise limited scattering spectrum,[1,3] and (2) conventional scanning Raman with increased signal generation via enormously increased source power.[2] In either case the motivation has been to enhance the analytical utility of normal Raman spectroscopy by exciting so far to the red that interferences from sample or impurity fluorescence are avoided.

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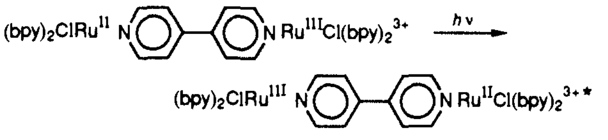
This approach succeeds of course because electronic transitions are increasingly uncommon as one moves to energies below those of the visible region.

In this study, just the opposite approach has been taken. Rather than employing near-IR irradiation to avoid electronic excitation, we have intentionally sought to achieve resonance in the near-infrared. The electronic transitions of interest were low-lying intervalence (metal-to-metal) charge transfers, e.g. eq 1.[4] Our



(1)

bpy = 2, 2'-bipyridine

hope was that laser excitation near λ_{max} for eq 1 would lead to intervalence-enhanced Raman scattering by an electronic resonance mechanism (Albrect "A-term" resonance). We have recently shown experimentally that relative scattering intensities for pre- or postresonance Raman can be used to obtain quantitative, mode-specific information about the vibrational Franck–Condon barrier to intervalence charge transfer.[5a] Furthermore, when coupled with either a normal-coordinate analysis or an appropriate local-mode approximation, the intensities can yield quantitative estimates of redox-induced bond distortions.[5,6] The background theory and analytical formulae for the earlier work came from the time-dependent semiclassical treatment of scattering devised by Heller and others.[7,8] In our earlier study[5a] the mixed-valence chromophore was $(NC)_5Ru^{II}$–CN–$Ru^{III}(NH_3)_5^-$. In this molecule, coordinative asymmetry at the electron-trapping sites leads to significant redox asymmetry (ca. 0.9 V) and, consequently, a shift of the intervalence transition into the visible region (λ_{max} = 684 nm in unbuffered water[9]). This, in turn, permits conventional Raman instrumentation to be employed.

In the present study, we instead investigated three dimers lacking redox asymmetry. The specific systems were $(bpy)_2ClRu$-4,4'-bpy-$RuCl(bpy)_2^{4+/3+/2+}$ (**1**), $(H_3N)_5Ru$-4,4'-bpy-$Ru(NH_3)_5^{6+/5+/4+}$ (**2**), and $(NC)_5Fe$-4,4'-bpy-$Fe(CN)_5^{4-/5-/6-}$ (**3**), where bpy is 2,2'-bipyridine and 4,4'-bpy is 4,4'-bipyridine. As noted above, these systems display broad intervalence transitions in the near-IR region (λ_{max} = 985, 1035, and 1250 nm for **1**, **2**, and **3**, respectively). They are nearly ideally configured, therefore, for resonant excitation at 1064 nm with a Nd:YAG laser source.

The motives for investigating symmetrical systems by resonance Raman spectroscopy were three: First, there is an obvious and compelling analogy between symmetrical intervalence charge transfer (optical or thermal) and well-studied bimolecular electron self-exchange processes.[4] That analogy could be quantitatively explored if appropriate Raman-generated Franck–Condon parameters were available. Second, the vast majority of interesting molecular systems for which intervalence transitions can be cleanly observed are symmetrically configured, with identical trapping sites and coordination environments. As noted above, this tends to place the intervalence absorption transitions in the near-infrared. It is important, therefore, to discover whether resonance (intervalence) Raman can be implemented for such systems as a routine and general spectroscopic tool. Third, there are bothersome technical complications in the time-dependent scattering analysis that are manifest whenever Duschinsky rotation (excited-state mode mixing) occurs.[10] One way to avoid such complications might be to focus on transitions (like eq 1) for which the ground and excited electronic states are, because of molecular symmetry, completely equivalent (apart from vibrational excitation).

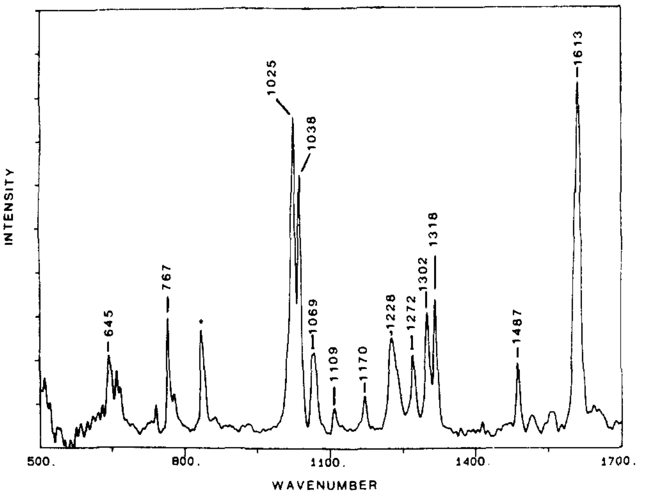


Figure 1. Near-infrared (λ_{ex} = 1064 nm) Fourier-transform Raman spectrum of ca. 7–15 mM $(bpy)_2ClRu^{II}$-4,4'-bpy-$Ru^{III}Cl(bpy)_2^{3+}$ in CD_3CN (solvent spectrum subtracted; stars denote residual solvent peaks).

Experimental Section

The fully reduced (M(II)–M(II)) forms of the three dimeric complexes were prepared and purified according to literature methods.[11-13] The fully oxidized dimer, $[(bpy)_2ClRu^{III}$-4,4'-bpy-$Ru^{III}Cl(bpy)_2](PF_6)_4$, was obtained by first metathasizing the doubly reduced hexafluorophosphate salt to the chloride with tetrabutylammonium chloride in acetone. The chloride salt was dissolved in water (slightly acidified with HCl) and oxidized by the addition of aqueous ceric ammonium nitrate. The fully oxidized PF_6^- salt was recovered by addition of concentrated NH_4PF_6 solution. The filtered pale-yellow solid was dissolved in a minimum of acetone, insoluble material was filtered off, and the Ru(III)–Ru(III) form was finally recovered by addition of the filtrate to excess stirring ether. The fully oxidized form of **2** was prepared in a similar manner, except the dimer was recovered from the oxidizing solution as the pale-yellow chloride by addition of excess acetone. The oxidized form of **3** was prepared by addition of excess Br_2 vapor to an aqueous solution of the dimer. The green solid was isolated by evaporating the solution to dryness. The mixed-valence M(II)–M(III) forms of the dimers were prepared in solution via the comproportionation reaction of nearly equal molar amounts of the M(II)–M(II) and M(III)–M(III) forms. A slight excess of the III–III form was added to diminish the amount of II–II present from disproportionation (see below).

Fourier-transform Raman spectra were taken of $[(bpy)_2ClRu^{II}$-4,4'-bpy-$Ru^{III}Cl(bpy)_2](PF_6)_3$ in CD_3CN with use of 400 mW of incident 1064-nm light with 4-cm^{-1} resolution on previously described instrumentation.[1] (Deuterated solvents were used in order to avoid possible heating and thermal lensing effects associated with C–H overtone excitation.) Scanning Raman spectra were taken (or attempted) for the three dimers in each of their valence forms (II–II, II–III, and III–III). Spectra were obtained with 24-cm^{-1} resolution with use of a 90° scattering geometry with 800 mW of 1064-nm light incident on a glass capillary sample tube. The details of the scanning Raman apparatus have also been described previously.[2] Typical samples were 7 mM solutions of $(bpy)_2ClRu$-4,4'-bpy-$RuCl(bpy)_2^{4+/3+/2+}$ in CD_3CN and 8 mM solutions of $(H_3N)_5Ru$-4,4'-bpy-$Ru(NH_3)_5^{6+/5+/4+}$ in D_2O. Spectra for dimer 3

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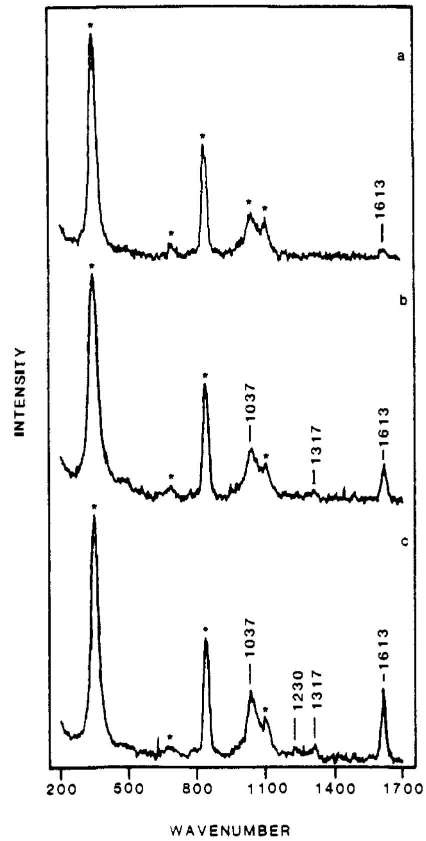

Figure 2. Near-infrared (λ_{ex} = 1064 nm) scanning Raman spectra of 7 mM $(bpy)_2ClRu$-4,4′-bpy-$RuCl(bpy)_2{}^{n+}$ in CD_3CN: (a) n = 4 (solvent peaks indicated by stars), (b) n = 3, (c) n = 2.

could not be obtained due to thermal degradation of the sample at all concentrations tried (from 15 mM to 1 mM in D_2O). Additional spectra of $(H_3N)_5Ru$-4,4′-bpy-$Ru(NH_3)_5{}^{4+}$ were obtained with visible excitation at 647.1 nm by using a system described previously.[5b]

Results and Discussion

An FT-Raman scan of $(bpy)_2ClRu^{II}$-4,4′-bpy-$Ru^{III}Cl(bpy)_2{}^{3+}$ in CD_3CN is shown in Figure 1. Essentially identical results (albeit, with lower resolution) were obtained with the scanning instrument (see Figure 2b). Note that the excitation wavelength in either case is nearly coincident with λ_{max}(MMCT). In the figure, the peak positions and especially the relative peak intensities indicate (following earlier assignments[14]) that the observed bands are due to ring deformations of the bridging ligand (4,4′-bipyridine). Figure 2a displays the scanning Raman spectrum for $(bpy)_2ClRu^{III}$-4,4′-bpy-$Ru^{III}Cl(bpy)_2{}^{4+}$. The spectrum is striking in that only a single band appears (1613 cm^{-1}). Furthermore, the band is much weaker here than it is in the mixed-valence chromophore. (In both cases intensities are measured versus acetonitrile as an internal reference.) Figure 2c completes the picture; it shows the scanning Raman spectrum for the Ru(II)-Ru(II) form. The pertinent findings are as follows: (1) The fully reduced dimer displays the full complement of 4,4′-bpy modes, although the 2,2′-bpy modes again are missing. (2) The scattering is actually more intense here (Figure 2c) than it is in the mixed-valence dimer (Figure 2b), despite the lack of a resonant intervalence transition in the fully reduced chromophore.

It is worth noting that the $(H_3N)_5Ru$-4,4′-bpy-$Ru(NH_3)_5{}^{6+/5+/4+}$ system (Figure 3) tells a similar story. The scanning Raman spectrum for Ru(III)-Ru(III) in 0.5 M Na_2SO_4/D_2O is exceedingly weak (only the $SO_4{}^{2-}$ reference peak at 981 cm^{-1} is seen). Scattering is stronger for Ru(III)-Ru(II), and for Ru(II)-Ru(II) it is stronger yet. The spectra are again dominated by 4,4′-bpy modes, although a Ru-N(bpy) stretch (391 cm^{-1}) is also seen.

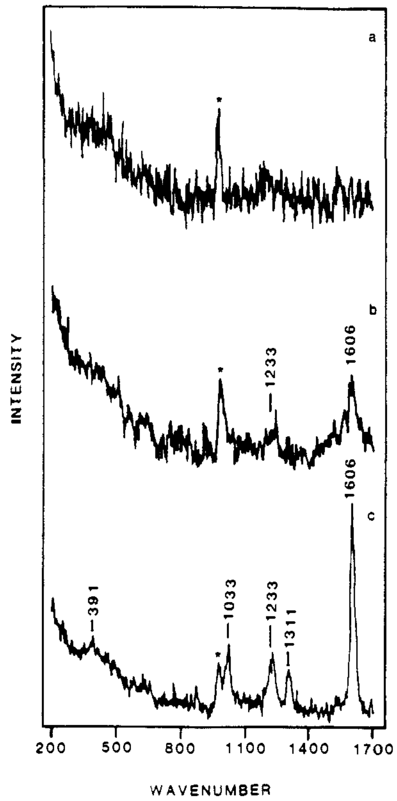

Figure 3. Near-infrared (λ_{ex} = 1064 nm) scanning Raman spectra of 8 mM $(H_3N)_5Ru$-4,4′-bpy-$Ru(NH_3)_5{}^{n+}$ + 0.5 M Na_2SO_4 in D_2O: (a) n = 6, (b) n = 5, (c) n = 4 (a star denotes the $SO_4{}^{2-}$ reference peak at 981 cm^{-1}).

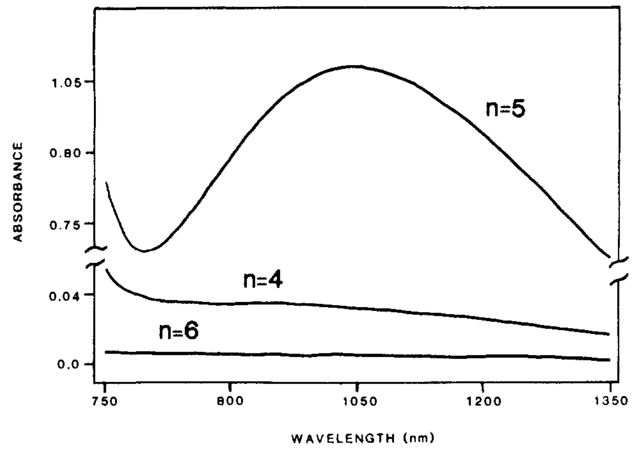

Figure 4. Near-infrared absorption spectra for $(H_3N)_5Ru$-4,4′-bpy-$Ru(NH_3)_5{}^{n+}$ in D_2O. (Note the expanded absorbance scale for n = 4 and 5.)

The intensity progressions in the two valence-series experiments (Figures 2 and 3) clearly show that for both systems some form of electronic enhancement exists. (Note that in each case the Ru(III)-Ru(III) form is completely nonchromophoric at 1064 nm (see Figure 4)). The observation that the enhancement is greater in both instances for the Ru(II)-Ru(II) form than for the mixed-valent Ru(II)-Ru(III) rules out an intervalence resonance (cf. eq 1) as the predominant cause of the enhancement effect. Instead the enhancements seem to be due to preresonance with Ru(II)-to-bridge transitions. Figure 4 indeed shows that the tail of this transition extends out to 1064 nm in the absorption spectrum for $(H_3N)_5Ru^{II}$-4,4′-bpy-$Ru^{II}(NH_3)_5{}^{4+}$. Additional evidence for metal-to-bridge enhancement is provided by Raman spectra of $(H_3N)_5Ru^{II}$-4,4′-bpy-$Ru^{II}(NH_3)_5{}^{4+}$ obtained at 647 nm (i.e. closer to resonance). These spectra show the same intensity

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[14] See, for example, spectra representative of coordinated 4,4′bpy: a) Caswell, D. S.; Spiro, T. G. *Inorg. Chem.*, 1987, *26*, 18, and by contrast, those representative of coordinated 2,2′-bpy: (b) McClanahan, S.; Kincaid, J. *J. Raman Spectrosc.* **1984**, *15*, 173.

patterns as do those obtained in the near-IR. This strongly suggests that the observed resonance enhancements at different excitation energies emanate from a common electronic transition.[15]

One further question concerning chromophore identity needs to be addressed for the near-infrared experiments: Given the finite occurrence of at least some disproportionation (i.e., 2(II–III) $\rightleftarrows$ II–II + III–III) might not the observed "mixed-valence" Raman enhancements (Figures 2b and 3b) arise instead from resonant excitation of minority (Ru(II)–Ru(II)) species? A consideration of comproportionation equilibria provides some insight. For the decaammine complex the comproportionation constant is 20;[16] for (bpy)ClRu^{II}-4,4′-bpy-Ru^{III}Cl(bpy)$_2^{3+}$ it is 15.[17] Taking into account the presence of intentionally added Ru(III)–Ru(III) species (see above), the Ru(II)–Ru(II):Ru(II)–Ru(III) ratio in both experiments is 1:5. This ratio clearly is too low to accommodate the approximately 1:2 ratios of scattering intensity in Figure 2b vs Figure 2c and in Figure 3b vs Figure 3c. It follows then—in both mixed-valence experiments—that Ru(II)–Ru(III) species must be the dominant near-infrared chromophores.

Two other points merit discussion. The first is the observation of essentially complete coincidence of vibrational frequencies for the Ru(II)–Ru(II) vs Ru(II)–Ru(III) species (see Figures 2 and 3). In view of the overall differences in oxidation state, one might have naively anticipated substantial frequency differences for the two types of species. It needs to be appreciated, however, that the scattering chromophore in all cases is the Ru^{II}-4,4′-bpy fragment. Furthermore the metal sites in both dimers are held fairly far apart by the bridging ligand (ca. 11-Å separation). Evidently the distance is great enough to mitigate against "remote site" perturbations of internal vibrations.

The second point is that in both $(H_3N)_5Ru^{II}$-4,4′-bpy-$Ru^{III}(NH_3)_5^{5+}$ and $(bpy)_2ClRu^{II}$-4,4′-bpy-$Ru^{III}Cl(bpy)_2^{3+}$, metal-to-bridge enhancement seems at first glance to be surprisingly dominant over metal-to-metal enhancement—especially in view of the relative near-infrared extinctions. There are at least three possible explanations. First, of course, only the metal-to-bridge transition should lead to enhanced bridge-based scattering. Second, because the relative intensities are anticipated to be weighted by the squares of the vibrational frequencies,[7] the high-frequency bridge-localized modes will tend to be more prominent than lower frequency metal–ligand modes, even when the relevant normal mode displacements are of comparable magnitude. Finally, there may indeed be some intervalence contribution to low-frequency mode enhancement. For these particular modes our preliminary experiments really serve only to implicate the metal-to-bridge enhancement mechanism; they do not necessarily rule out other sources of enhancement.

To summarize, clear evidence has been found for resonance enhancement of Raman scattering in the near infrared for two mixed-valence ions and their fully reduced congeners. The enhancements are due, however, to metal-to-ligand rather than metal-to-metal transitions. The search for intervalence enhancement in the near-IR would probably most profitably be directed toward (1) chromophores that can be excited even further to the red where metal-to-ligand tailing is unlikely,[18] (2) chromophores lacking interfering metal-to-ligand charge-transfer transitions—for example, the nearly symmetrical dimer $(NC)_5Fe^{III}$–NC–$Fe^{II}(CN)_5^{6-}$, and/or (3) chromophores featuring very prominent low-energy modes (e.g. metal–ligand vibrations). These modes are the one most likely, of course, to be affected strongly by metal-to-metal charge transfer. Unfortunately, they are not easily observed with the current high-resolution FT instrument because of the nature of the filters required for efficient rejection of Rayleigh scattering. Such modes might be detectable, however, with the lower resolution scanning instrument. (Note, for example, the low-energy Ru–N stretch detected in Figure 3c.)

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Supplementary Material Available: Figure showing visible region absorption spectra for $(bpy)_2ClRu$-4,4′bpy-$RuCl(bpy)_2^{5+/4+/3+}$ and a table giving absorption maxima and extinction coefficients (2 pages). Ordering information is given on any current masthead page.

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(15) Note also that the metal-to-bridge resonance mechanism provides an obvious rationale for the lack of detectable scattering from coordinated 2,2′-bipyridine (Figure 2b).

(16) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(17) The comproportionation constant for this dimer was calculated from the difference in formal potentials for the 4+/3+ and 3+/2+ couples. These were obtained, in turn, by comparing experimental cyclic voltammograms with those generated by digital simulation (Doorn, S. K., unpublished).

(18) Appropriate excitation sources might include *f*-center lasers ($\lambda_{ex} \approx$ 1.4 to 1.6 μm), alternative Nd:YAG lasers featuring 1.32-μm output, or a pulsed Nd:YAG laser (1.064 μm) coupled to a Raman shifter (for example, $\lambda_{ex} \approx$ 1.5 μm based on the lowest D_2 Stokes line).