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Resonance-Enhanced Raman Scattering in the Near-Infrared Region. Preliminary Studies of Charge Transfer in the Symmetric Dimers

$(2,2'\text{-bpy})_2\text{ClRu-4,4'-bpy-RuCl}(2,2'\text{-bpy})_2^{4+/3+/2+}$,
 $(\text{H}_3\text{N})_5\text{Ru-4,4'-bpy-Ru}(\text{NH}_3)_5^{6+/5+/4+}$, and
 $(\text{NC})_5\text{Fe-4,4'-bpy-Fe}(\text{CN})_5^{4-/5-/6-}$

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208, Department of Chemistry, The University of Texas, Austin, Texas 78712, and Central Research and Development, E. I. du Pont de Nemours and Co., Experimental Station, E328/126, Wilmington, Delaware 19898. Received May 8, 1989

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 $(2,2'\text{-bpy})_2\text{ClRu-4,4'-bpy-RuCl}(2,2'\text{-bpy})_2^{4+/3+/2+}$, $(\text{H}_3\text{N})_5\text{Ru-4,4'-bpy-Ru}(\text{NH}_3)_5^{6+/5+/4+}$, and $(\text{NC})_5\text{Fe-4,4'-bpy-Fe}(\text{CN})_5^{4-/5-/6-}$. 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 spec-

trum,^{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.

(1) (a) Hirschfeld, T.; Chase, D. B. *Appl. Spectrosc.* **1986**, *40*, 133. (b) Chase, D. B. *J. Am. Chem. Soc.* **1986**, *108*, 7485. (c) Chase, D. B. *Anal. Chem.* **1987**, *59*, 881A.

(2) Porterfield, D. R.; Campion, A. *J. Am. Chem. Soc.* **1988**, *110*, 408.

(3) Zimba, C. G.; Hallmark, V. M.; Swalen, J. D.; Rabolt, J. F. *Appl. Spectrosc.* **1987**, *41*, 721.

(4) For a review, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

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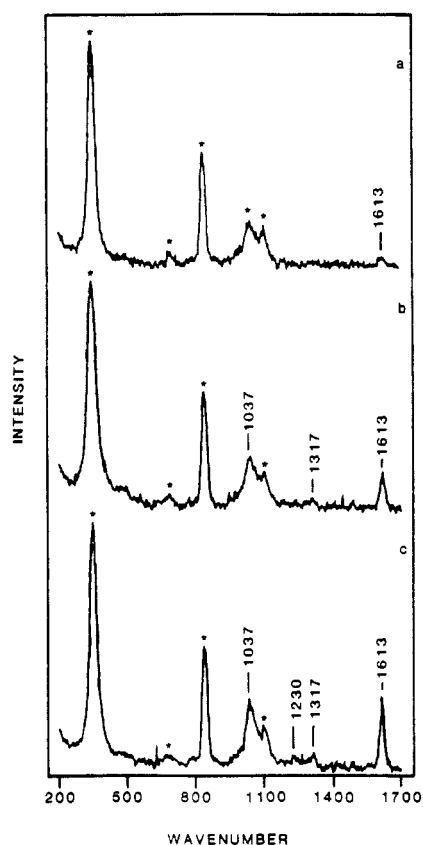


Figure 2. Near-infrared ($\lambda_{\text{ex}} = 1064$ nm) scanning Raman spectra of 7 mM $(\text{bpy})_2\text{ClRu-4,4'-bpy-RuCl(bpy)}_2^{n+}$ in CD_3CN : (a) $n = 4$ (solvent peaks indicated by stars), (b) $n = 3$, (c) $n = 2$.

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 $(\text{H}_3\text{N})_5\text{Ru-4,4'-bpy-Ru}(\text{NH}_3)_5^{4+}$ were obtained with visible excitation at 647.1 nm by using a system described previously.^{5b}

Results and Discussion

An FT-Raman scan of $(\text{bpy})_2\text{ClRu}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{III}}\text{Cl(bpy)}_2^{3+}$ 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 $\lambda_{\text{max}}(\text{MMCT})$. In the figure, the peak positions and especially the relative peak intensities indicate (following earlier assignments¹⁴) that the observed bands are due to ring deformations of the bridging ligand (4,4'-bipyridine). Figure 2a displays the scanning Raman spectrum for $(\text{bpy})_2\text{ClRu}^{\text{III}}\text{-4,4'-bpy-Ru}^{\text{II}}\text{Cl(bpy)}_2^{4+}$. 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 $\text{Ru}(\text{II})\text{-Ru}(\text{II})$ 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 $(\text{H}_3\text{N})_5\text{Ru-4,4'-bpy-Ru}(\text{NH}_3)_5^{6+/5+/4+}$ system (Figure 3) tells a similar story. The scanning Raman spectrum for $\text{Ru}(\text{III})\text{-Ru}(\text{III})$ in 0.5 M $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$ is exceedingly weak (only the SO_4^{2-} reference peak at 981 cm^{-1} is seen). Scattering is stronger for $\text{Ru}(\text{III})\text{-Ru}(\text{II})$, and for $\text{Ru}(\text{II})\text{-Ru}(\text{II})$ it is stronger yet. The spectra are again

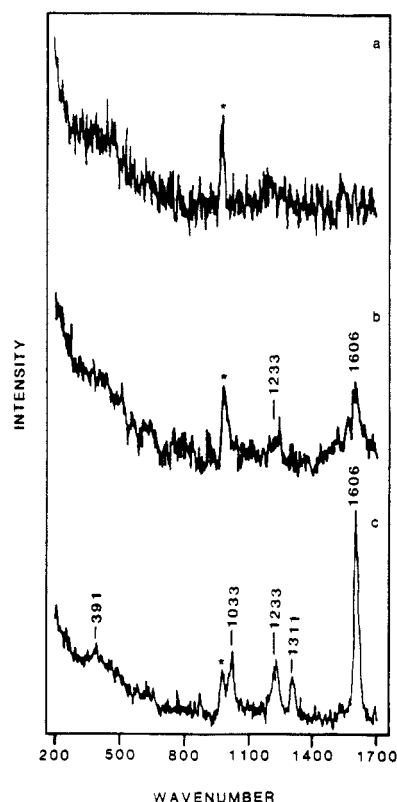


Figure 3. Near-infrared ($\lambda_{\text{ex}} = 1064$ nm) scanning Raman spectra of 8 mM $(\text{H}_3\text{N})_5\text{Ru-4,4'-bpy-Ru}(\text{NH}_3)_5^{n+} + 0.5\text{ M Na}_2\text{SO}_4$ in D_2O : (a) $n = 6$, (b) $n = 5$, (c) $n = 4$ (a star denotes the SO_4^{2-} reference peak at 981 cm^{-1}).

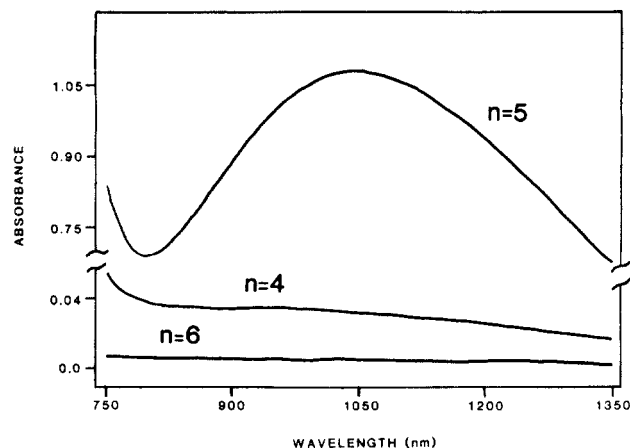


Figure 4. Near-infrared absorption spectra for $(\text{H}_3\text{N})_5\text{Ru-4,4'-bpy-Ru}(\text{NH}_3)_5^{n+}$ in D_2O . (Note the expanded absorbance scale for $n = 4$ and 5.)

dominated by 4,4'-bpy modes, although a Ru-N(bpy) stretch (391 cm^{-1}) is also seen.

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 $\text{Ru}(\text{III})\text{-Ru}(\text{III})$ form is completely nonchromophoric at 1064 nm (see Figure 4)). The observation that the enhancement is greater in both instances for the $\text{Ru}(\text{II})\text{-Ru}(\text{II})$ form than for the mixed-valent $\text{Ru}(\text{II})\text{-Ru}(\text{III})$ 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 $\text{Ru}(\text{II})\text{-to-bridge}$ transitions. Figure 4 indeed shows that the tail of this transition extends out to 1064 nm in the absorption spectrum for $(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{II}}(\text{NH}_3)_5^{4+}$. Additional evidence for metal-to-bridge enhancement is provided by Raman spectra of $(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{II}}(\text{NH}_3)_5^{4+}$ obtained at 647 nm (i.e. closer to resonance). These spectra show the same intensity

(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. *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., $2(\text{II-III}) \rightleftharpoons \text{II-II} + \text{III-III}$) 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 $(\text{bpy})_2\text{ClRu}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{III}}\text{Cl}(\text{bpy})_2^{3+}$ it is 15.¹⁷ Taking into account the presence of intentionally added Ru(III)-Ru(III) species (see above), the $\text{Ru(II)-Ru(II)}:\text{Ru(II)-Ru(III)}$ 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 $\text{Ru}^{\text{II}}\text{-4,4'-bpy}$ 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 $(\text{H}_3\text{N})_5\text{Ru}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{III}}\text{-(NH}_3)_5^{5+}$ and $(\text{bpy})_2\text{ClRu}^{\text{II}}\text{-4,4'-bpy-Ru}^{\text{III}}\text{Cl}(\text{bpy})_2^{3+}$, 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 $(\text{NC})_5\text{Fe}^{\text{III}}\text{-NC-Fe}^{\text{II}}(\text{CN})_5^{6-}$, 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 $(\text{bpy})_2\text{ClRu-4,4'-bpy-RuCl}(\text{bpy})_2^{5+/4+/3+}$ and a table giving absorption maxima and extinction coefficients (2 pages). Ordering information is given on any current masthead page.

(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 ($\lambda_{\text{ex}} \approx 1.4$ to $1.6 \mu\text{m}$), alternative Nd:YAG lasers featuring $1.32\text{-}\mu\text{m}$ output, or a pulsed Nd:YAG laser ($1.064 \mu\text{m}$) coupled to a Raman shifter (for example, $\lambda_{\text{ex}} \approx 1.5 \mu\text{m}$ based on the lowest D_2 Stokes line).