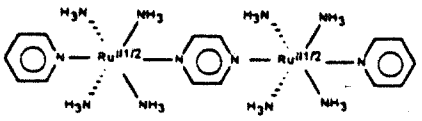
RESONANCE RAMAN IN THE EXTENDED NEAR INFRARED: EXPERIMENTAL TIME DEPENDENT SCATTERING STUDIES OF MIXED-VALENCE SYSTEMS

Vladimir I. Petrov[1], Robert D. Williams, and Joseph T. Hupp*

Dept. of Chemistry, Northwestern University, Evanston, IL 60208 U.S.A.
[1]Permanent address: S. I. Vavilov State Optical Institute, St. Petersburg, Russia

Nonresonant Raman spectroscopy in the near infrared (NIR) has become popular because of its ability to eliminate fluorescence interferences. These interferences are absent because electronic transitions (usually) are not found at such low energies. Low energy electronic transitions do exist, however, for an important class of electron transfer model compounds, namely, symmetrical mixed-valence ions [1]. These ions can exist either in localized (discrete valence; class II) or delocalized (averaged valence; class III) form, where the form obtained depends on the relative strengths of localizing (vibrational and solvational) versus delocalizing (electronic) forces. In principle, Raman spectroscopy can provide unique quantitative insight into the key vibrational factors defining the electronic form. Toward that end, we have recently shown that resonance Raman spectroscopy can be implemented in the *extended* NIR (1320 nm excitation) for dilute solutions (ca. 2 to 8 *mM*) of both class II and class III chromophores [2-4], despite ν^4 effects and severe detector noise problems. Here we describe the resonance Raman spectroscopy of a delocalized mixed-valence ion (**1**) that can be reversibly converted to localized form via partial encapsulation [5] and supramolecular symmetry reduction by a polyether macrocycle such as dibenzo-36-crown-12 (**2**). To motivate the quantitative interpretation of the spectroscopy we make extensive use of a time-dependent overlap (gaussian wavepacket propagation) methodology popularized by Heller [6].



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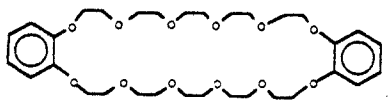

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Figure 1 shows uncorrected resonance Raman spectra (1320 and 1337 nm excitation) for **1** (lower curve) and **1**•crown (upper curve) in nitromethane-d_3 as solvent. The former is dominated by peaks corresponding to symmetric displacements along the metal-bridging ligand (pyrazine)-metal axis. As we have noted elsewhere for a related chromophore [3,4], enhancement of pyrazine modes

A more quantitative description of vibrational coupling to the NIR electronic transition can be obtained by using a time dependent scattering analysis. In this analysis, the scattering or polarizability tensor can be related to the half Fourier transform of the overlap of a vibrational wavepacket ($\phi(t)$) moving on the initial (i.e. upper) electronic surface and an excited vibrational wavefunction (ϕ) on the final (lower) electronic surface:

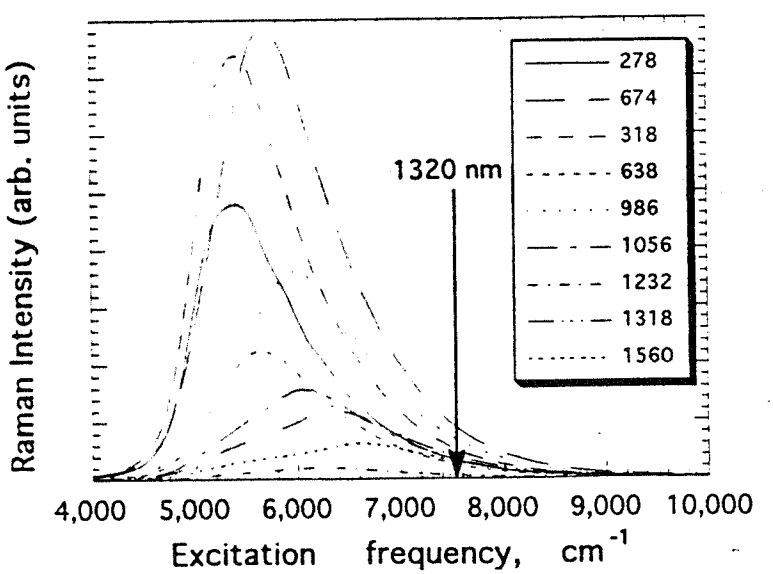
$$<\phi/\phi(t)> = \prod_k \{ \exp [-\frac{\Delta_k^2}{2} (1-\exp(-i\omega_k t)] \times (1-\exp(-i\omega_k t))^{n_k}$$

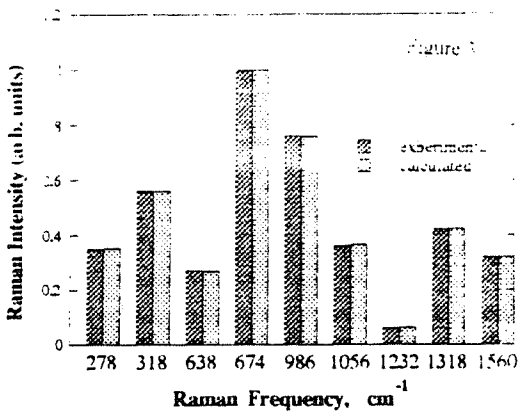
$$\times \frac{(-1)^{n_k}\Delta_k^{n_k}}{(2^{n_k}n_k!)^{1/2}} \} \exp(-i\omega_0 t) \times \exp(i\omega t - \Gamma t - i\chi_s t - \chi_s kTt^2) \qquad (2)$$

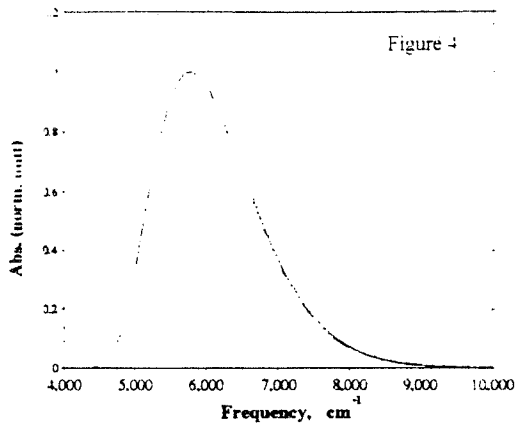
where Δ is a unitless normal coordinate displacement, ω_k are the frequencies of the normal modes, Γ is a phenomenological damping factor, χ_s is the solvent reorganization energy, and n_k is a term dealing with vibrational state. The corresponding full Fourier transform of the overlap yields the electronic absorption spectrum.

Figure 2 shows Raman excitation profiles generated via eq. 2, where the pertinent adjustable parameters are the displacements for each normal mode. A slice through these profiles at λ_{exc} = 1320 nm yields calculated relative Raman intensities (figure 3) that are in excellent agreement with instrument-response-corrected experimental data. Figure 4 shows that the same parameters also provide reasonable agreement with the absorption spectrum, where the total reorganization energy (χ) is ca. 900 cm^{-1} and is almost exclusively vibrational (i.e. $\chi = 0.5\Sigma\, \Delta_j^2 \nu_j$).

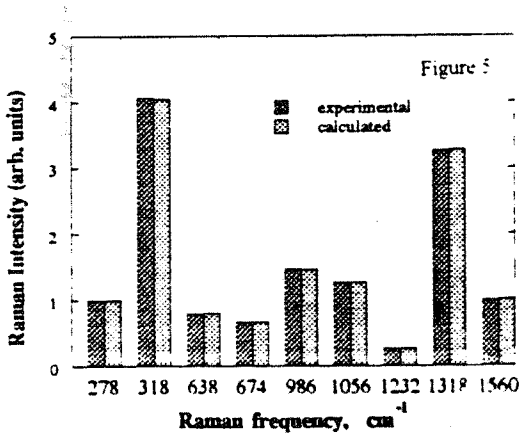
Figure 2

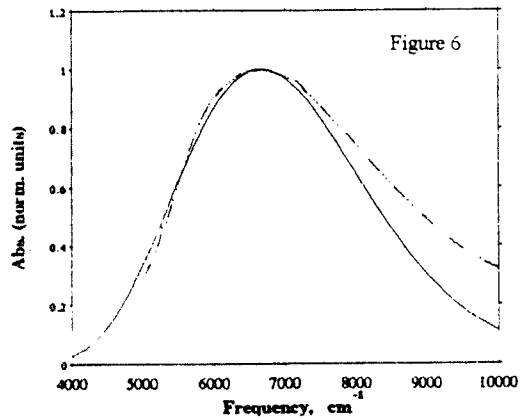






Figures 5 and 6 illustrate how the corrected scattering and absorption spectra transform following crown-induced valence localization. The time-dependent analysis shows that the total reorganization energy has: a) increased to ca. 3200 cm^{-1}, b) redistributed itself into modes that asymmetrically distort the bridge, and c) acquired a small, but significant solvent component. In summary, the Raman experiments and analysis provide the first clear experimental picture of how electronic delocalization (and subsequently localization) is induced and sustained in these unusual model compounds.





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