

Resonance Raman Studies in the Extended Near Infrared Region: Experimental Verification of a Three-Site Mixing Mechanism for Valence Delocalization in the Creutz–Taube Ion

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The Creutz–Taube (C–T) ion, $(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5^{5+}$ (**1**), was among the first intentionally prepared, molecular mixed-valency species. As a prototypical class III (i.e., electronically delocalized) system, it has been the subject of a large number of experimental,² as well as theoretical,^{3,4} investigations.⁵ Among the distinguishing properties of the ion are (1) identical or nearly identical metal–ligand (ML) bond lengths and bond angles at opposite ends of the molecule,² (2) a very large mixed-valence comproportionation constant,^{1,3c} and (3) an intense, narrow and somewhat asymmetric “intervalence absorption” feature in the extended near infrared region (Figure 1).¹ The intervalence transition is additionally characterized by an approximate solvent independence (implying little or no solvent reorganization following optical excitation)¹ and a negligible second-derivative Stark effect (implying little or no net charge-transfer character for the transition).^{3c} While there is now general agreement that these features describe a system exhibiting both ground- and excited-state electronic delocalization, there is significantly less agreement concerning the detailed nature of the delocalization phenomenon. These more specific issues can, however, be resolved by obtaining resonance Raman spectra in the C–T intervalence region (i.e., the extended NIR). We report the first such spectra. From the spectra we find compelling evidence for a three-site mechanism for valence delocalization, necessarily involving extensive, direct bridge orbital participation.

One limiting description of the valence delocalization process is based on a pair of zeroth-order states with the odd electron confined to a $d\pi$ Ru orbital on either the left- or right-hand side of the molecule.³ The states are vibronically coupled by an antisymmetric ML stretching motion (i.e., compression at one center, expansion at the other), resulting in the familiar double-well, ground potential energy (PE) surface. The addition of substantial electronic coupling necessarily mixes the states, eventually producing two new states (upper and lower delocalized states) with a single minimum on the PE surface for each. Intervalence absorption is then the optical process connecting the two. An important feature of this model is that displacements in symmetric modes (for example, bridge modes) cannot be

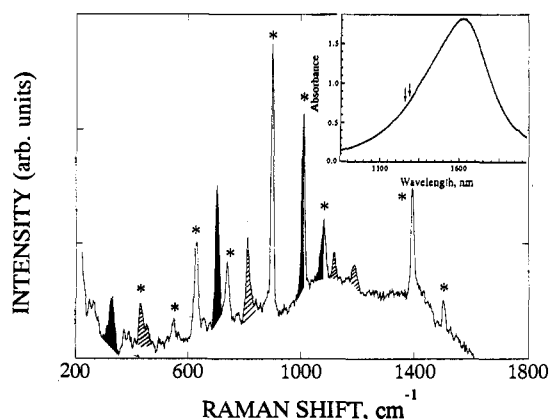
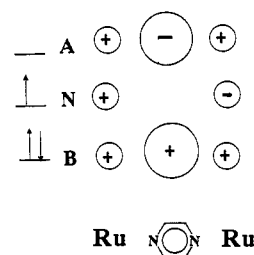


Figure 1. Dark peaks: resonance Raman spectrum of **1** with $\lambda_{\text{exc}} = 1320$ nm. Shaded: duplicative peaks from $\lambda_{\text{exc}} = 1337$ nm. Asterisks (*) indicate solvent peaks or reflections. Inset: absorption spectrum.

coupled to the intervalence transition and cannot play a direct role in the (de)localization process.

An alternative description takes into account strong back-bonding interactions⁶ between filled (or partially filled) $d\pi$ Ru orbitals and one or more empty π^* orbitals on the bridge. This interaction induces three-center mixing (Ru–pyz–Ru) and leads to three new molecular orbitals (based on one pyz π^* and two Ru d_{xz} parent orbitals; see below).^{4,7} The lowest of these is doubly occupied and is formally bonding; the next is nonbonding and half-occupied; the highest is antibonding and empty. The intervalence transition then is one which promotes an electron from the three-center bonding orbital to the nonbonding orbital. In the limit of strong electronic coupling, the nature of the transition becomes predominantly ligand to (double) metal charge transfer (LMCT), rather than metal-to-metal charge transfer. Additionally, explicit recognition of the (possible) role of the bridge in providing electronic coupling leads to a completely different picture of vibronic coupling. Most importantly, symmetric bridge displacements and symmetric metal–ligand displacements may now be directly coupled to intervalence excitation (as one might expect on the basis of the simple qualitative description of the process as a double LMCT excitation).



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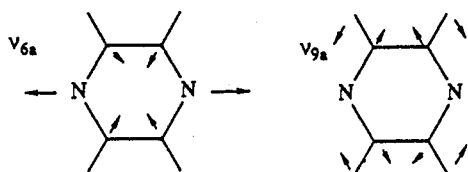
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powers (1.5–2 W) and by taking advantage of intervalence enhancement effects.

For samples in CD_3NO_2 , peaks appear at 1008 (partially obscured), 703, 334, and 326 cm^{-1} (Figure 1) based on 1320-nm excitation (Nd:YAG laser). The last three, at least, are polarized, suggesting that they originate from "A term" scattering. Control experiments at 1320 nm with the fully reduced (4+) and fully oxidized (6+) forms (i.e., nonabsorbing forms) and at 1064 nm (nonresonant) with the mixed-valence (5+) form confirm that scattering from the 5+ ion at 1320 nm is strongly resonance enhanced. The vibration at 703 cm^{-1} is assigned as the symmetric ν_{6a} mode of pyrazine,^{2a,10} while the vibrations at 334 and 326 cm^{-1} are assigned as Ru–N stretches.^{2a,10b} None of these is appreciably changed by replacement of NH_3 by ND_3 . With d_4 -pyz, however, the higher vibrations shift to 990 (polarized) and 680 cm^{-1} , while the lower vibrations apparently coalesce to give a broad peak at 325 cm^{-1} . The lowest frequency mode can be more precisely assigned, therefore, as an Ru–pyz stretch. Splitting of this mode in the nonlabeled pyz case (denoted by h_4 -pyz), however, is puzzling, especially if the ground electronic state is delocalized. We speculatively ascribe the splitting to a Fermi resonance interaction¹¹ (with an overtone or combination mode of unknown origin). Depending on the details of the interaction, a resonance effect could account for the apparent coalescence following isotopic perturbation. The feature at 990 cm^{-1} is tentatively assigned as the ν_1 breathing mode. An alternative assignment as a C–C–D bend seems unlikely on the basis of the observed H/D shift.



Finally, with d_4 -pyz, additional peaks appear at ~ 1316 and 1056 cm^{-1} . The former is probably a combination band ($990 +$

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(11) An alternative interpretation is that $\nu(326)$ and $\nu(332)$ represent two separate Ru–N(pyrazine) vibrations on a double-well, ground potential surface (i.e., chemically distinct (localized valence) metal sites exist). The intense peak at 703 cm^{-1} would then be assigned as ν_3 , a nontotally symmetric mode, where Raman activation would be permitted if a change in point group accompanied intervalence excitation. ($\nu(1008)$, however, would still be assigned as a symmetrical bridging vibration.) The primary difficulty with this interpretation is that it implies substantial net charge transfer (or dipole moment change) upon intervalence excitation, a suggestion seemingly inconsistent with recent electronic Stark effect studies.^{2c}

325). The latter, in retrospect, is also present for the compound containing h_4 -pyz, but is coincident with a solvent or reflection peak at 1084 cm^{-1} . It is tempting, on the basis of the IR spectrum of free pyrazine,^{10c} to assign this relatively weak mode as a nontotally symmetric mode (ν_{18} , out-of-plane bend?). (Alternatively, it could be any one of several energy-shifted, totally symmetric modes.) If the (speculative) assignment as nontotally symmetric is correct, it suggests that a slight change of molecular symmetry accompanies electronic excitation, which further suggests a slight change in extent of valence (de)localization with excitation.

Clearly the most striking feature of the experiment is the strong coupling of bridge motions to the intervalence transition. (Recall that resonance enhancement of a given vibrational mode generally implies displacement of that mode following electronic excitation.⁹) Coupling to a symmetric bridge mode (e.g., ν_{6a} or ν_1) implies direct involvement of one or more bridge orbitals in the intervalence excitation process. It also necessarily implies direct bridge participation in the delocalization process. We conclude, therefore, that three-site mixing (Ru–pyz–Ru), rather than conventional two-site coupling (Ru–Ru), is the operative mechanism for ground-state delocalization in **1**. The involvement of the Ru–N(pyrazine) stretching vibration¹² is also consistent with a three-site delocalization mechanism and with an intervalence process that resembles charge transfer from an effectively anionic bridge to a pair of approximately Ru(III) sites.^{4b}

While three-site mixing mechanisms have been discussed primarily in the context of fully delocalized systems, they can in principle play a significant role in coupling localized ligand-bridged valence sites,^{4a} a possibility we are currently investigating. We are also focusing on fits of intervalence line shapes to relative mode displacements (Raman derived) to obtain absolute ground-state/intervalence-excited-state vibrational structural changes. Finally, we are examining **1** and related species under conditions of local symmetry reduction and possible valence localization or partial localization (based on second-sphere binding of crown species^{2d}). Preliminary studies indicate that a drastic redistribution of intervalence-based Franck–Condon activity accompanies the binding.

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(12) Ru–N(pyrazine) displacement is also allowed in the two-site model (but as difference coordinate, rather than sum coordinate displacement).