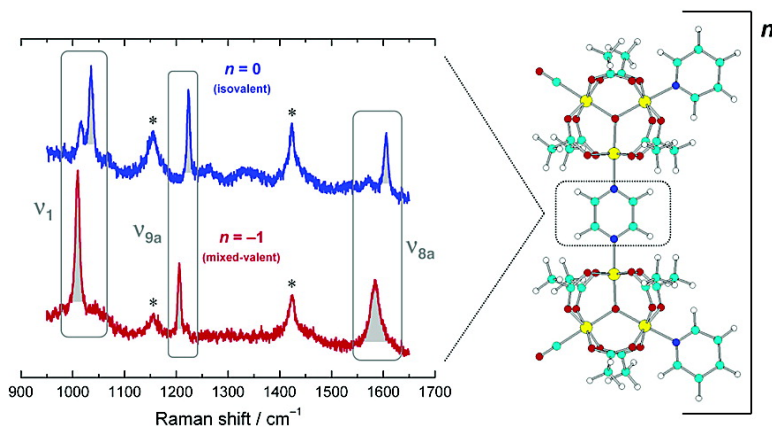Communication

Intervalence Involvement of Bridging Ligand Vibrations in Hexaruthenium Mixed-Valence Clusters Probed by Resonance Raman Spectroscopy

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Intervalence Involvement of Bridging Ligand Vibrations in Hexaruthenium Mixed-Valence Clusters Probed by Resonance Raman Spectroscopy

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The nature of electronic communication and delocalization in molecular mixed-valence species has been a subject of much investigation, particularly with respect to the Creutz−Taube ion, $[(NH_3)_5Ru]_2(pz)^{5+}$ (where pz = pyrazine) (**1**).[1] After much experimental investigation, including persuasive electroabsorption[2] and resonance Raman[3] experiments involving the near-infrared intervalence (IT) electronic absorption band, it was concluded that **1** is a delocalized, averaged-valence species (Robin−Day[4] class III) best described by a three-site vibronic coupling model[5−7] that explicitly includes an electronic state and vibrations of the bridging ligand. A versatile and more recently investigated pyrazine-bridged mixed-valence system is the "dimer" of trinuclear ruthenium clusters, $[(Ru_3O)(OAc)_6(CO)(\mathbf{L})]_2(pz)$ (Figure 1), where **L** = 4-(dimethy-
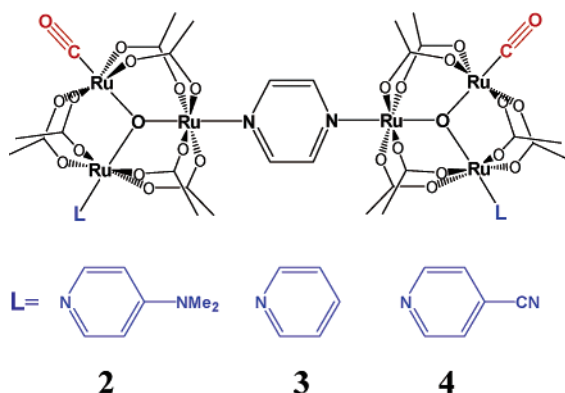

Figure 1. Ruthenium "dimers of trimers".

lamino)pyridine (**2**), pyridine (**3**), or 4-cyanopyridine (**4**). The electronic coupling between clusters can be tuned by different choices of the ancillary pyridyl ligand **L**, and dynamic effects of electron transfer (ET) on infrared vibrational spectra can be observed.[8,9] Resonance Raman spectra with excitation in the IT bands of these three ruthenium "dimers of trimers" are reported here. These data provide the first opportunity to explore how vibronic contributions of specific normal modes vary as electronic communication strength is systematically adjusted in mixed-valence compounds near the localized-to-delocalized transition. The results of this study are broadly applicable to understanding electronic and vibrational properties of mixed-valence compounds.

Figure 2 shows the Raman spectra[10] of **2**, **3**, and **4** as a function of oxidation state in a region that highlights three pyrazine-based Raman peaks. The excitation wavelength is not resonant in any electronic transition in the (0) isovalent oxidation states, but for the mixed-valence (−1) oxidation states the excitation is resonant with the transition previously assigned as the IT band, centered at
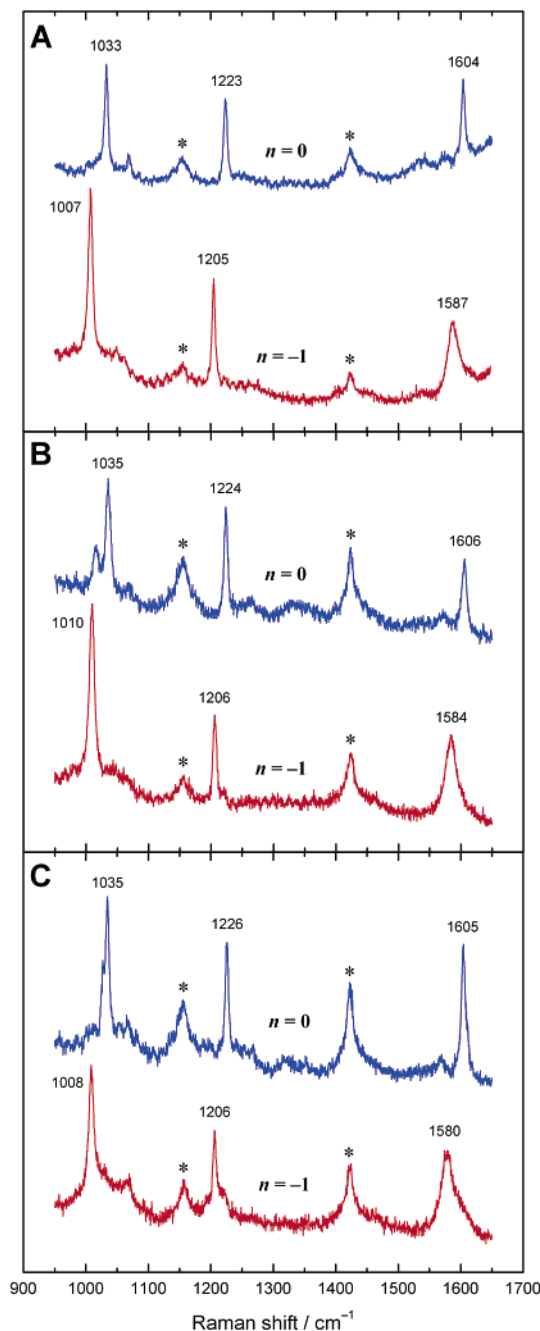

Figure 2. Raman spectra (λ_{exc} = 752 nm) of $\mathbf{2}^n$ (A), $\mathbf{3}^n$ (B), and $\mathbf{4}^n$ (C). Solvent peaks are marked by an asterisk (*), and minor peaks without labels are tentatively assigned to ancillary pyridyl ligand (**L**) modes.

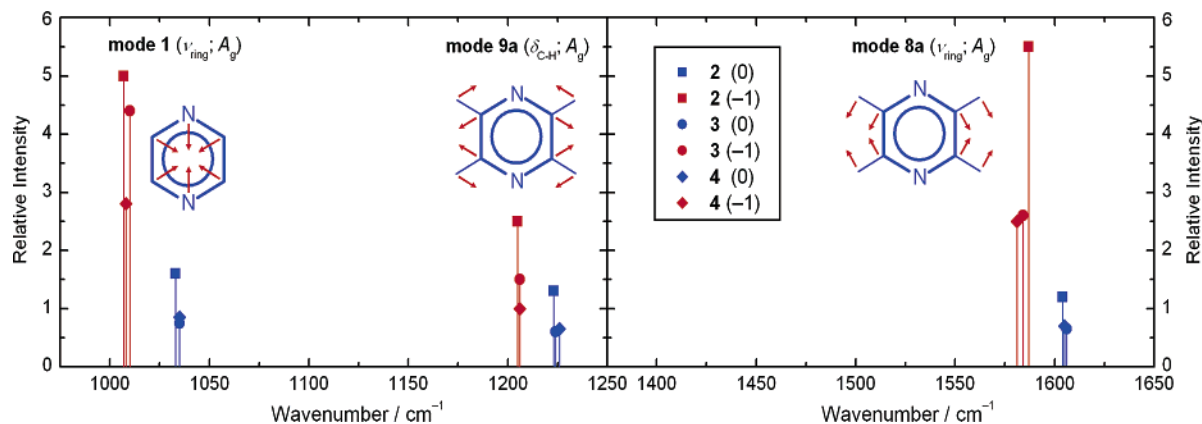† University of California.
‡ Los Alamos National Laboratory.

Figure 3. Stick graph showing the frequencies (for the ν_1, ν_{9a}, and ν_{8a} pyrazine modes) and peak intensities for clusters 2^n, 3^n, and 4^n (where $n = 0$ or -1). Integrated peak intensities are relative to solvent (CH_2Cl_2) peaks at 1157 cm^{-1} (ν_1 and ν_{9a}) and 1424 cm^{-1} (ν_{8a}). Estimated intensity uncertainties are ±10%.

approximately 830 nm.[8,9] Raman bands at 1035, 1225, and 1605 cm^{-1} in the neutral complexes are assigned to the ν_1, ν_{9a}, and ν_{8a} modes of pyrazine. Assignments were verified by comparison to analogous complexes with pyrazine-d_4 as bridging ligand[12] and noting the characteristic isotopic frequency shifts.[13,14]

Two trends are observed for these bands as a function of oxidation state. (i) All shift to lower frequency with more negative oxidation states. This is evidence of partial electronic occupation in the pyrazine π^* (LUMO) orbital in the (-1) oxidation state and suggests that electronic occupation on pyrazine is an important contributor to the electronic character of the mixed-valence state. (ii) Band intensities are enhanced in the (-1) state due to their coupling to the IT electronic transition. Vibronic coupling of such symmetric bridging ligand modes to the IT band (or the B $\rightarrow$ N transition) is predicted by the three-state model of Ondrechen.[5-7]

In 2^-, 3^-, and 4^-, enhancement of symmetric pyrazine bands varies with the electronic coupling between clusters (see Figure 3). Observed intensities follow the trend $2^- > 3^- > 4^-$, which is also the demonstrated trend in comproportionation constants and estimated intercluster ET rates.[8,9] The trend in intensities may reflect multiple factors. In the series 2^-, 3^-, 4^-, the maximum of the IT band shifts to longer wavelength and loses spectral intensity while the bandwidth increases. Changes in bandwidth likely reflect changes in vibronic coupling patterns and strengths, which would also influence resonance Raman responses. Quantitative resolution of the exact sources of the intensity enhancement patterns observed here will require more complete multiwavelength excitation profile experimental studies and detailed modeling of the Raman results.

A qualitative difference between the resonance Raman results for 2^-, 3^-, and 4^- and those for **1** is the absence of enhancement in nontotally symmetric bridging ligand modes in 2^-–4^-: For **1**, intensity in nontotally symmetric pyrazine modes at 1078, 1316, and 1412 cm^{-1} was observed,[3] but no peaks are seen near these frequencies in the spectra of the mixed-valence compounds shown in Figure 2. Prediction of enhancement strengths for nontotally symmetric modes for mixed-valence compounds near the localized-to-delocalized transition is a subject that requires detailed theoretical analysis, but the results reported here along with the previously reported results for **1** will provide important guidance for the understanding of vibronic contributions of nontotally symmetric vibrations in such cases. This is particularly true in light of the independent evidence available from the carbonyl IR spectra for compounds 2^-–4^- that provide estimates for the degree of charge localization.[8,9]

It is clear that a model which fully incorporates the electronic and vibrational participation of the bridging ligand must be invoked to explain the vibronic coupling of symmetric pyrazine modes to

the IT band, both in **1** and in 2^-–4^-. As is evident in infrared,[12] Raman, and bridge-substituent[15] studies of ruthenium "dimers of trimers", the importance of the mediating species in a full understanding of electron transfer and delocalization between strongly coupled sites should not be underestimated. These new results further demonstrate that resonance Raman spectra (and the vibronic coupling information found therein) can be obtained as a function of tunable electronic coupling. Analysis of coupling-dependent Raman results will increase the understanding of electronic structure and vibronic effects in bridge-mediated electron-transfer systems and will help address incompletely understood vibronic coupling issues at the localized-to-delocalized transition.

Supporting Information Available: Table of frequencies and intensities in spectra from Figures 2 and 3; table of peak assignments in pyrazine-d_4 species; electronic spectra of 2^-, 3^-, and 4^- with Raman excitation frequency noted (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Raman excitation was carried out using $\lambda_{exc} = 752$ nm from a Ti-sapphire laser operating at approximately 15 mW power. All solutions were ca. 1 mM sample and 0.1 M (NBu$_4$)PF$_6$ (supporting electrolyte) in CH$_2$Cl$_2$. The oxidation state was controlled using a modified version of a home-built spectroelectrochemical cell (see ref 11) with a fused silica window and a 4 mm diameter Pt working electrode, operating at room temperature. Raman spectra were collected using a backscattering geometry. Only the neutral (0) and mixed-valence (-1) oxidation states were sufficiently stable to collect Raman spectra at experimental temperatures. A lower-frequency symmetric pyrazine mode, ν_{6a} ($\nu \approx 700$ cm^{-1}), was overlapped with a solvent peak and could not be investigated quantitatively.
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