

## Solvent Control of Vibronic Coupling upon Intervalence Charge Transfer Excitation of $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$ as Revealed by Resonance Raman and Near-Infrared Absorption Spectroscopies

Chengfei Wang,<sup>†</sup> Brian K. Mohney,<sup>†</sup> Robert D. Williams,<sup>‡</sup> Vladimir Petrov,<sup>‡</sup> Joseph T. Hupp,<sup>‡</sup> and Gilbert C. Walker<sup>\*†</sup>

Department of Chemistry, University of Pittsburgh  
Pittsburgh, Pennsylvania 15260

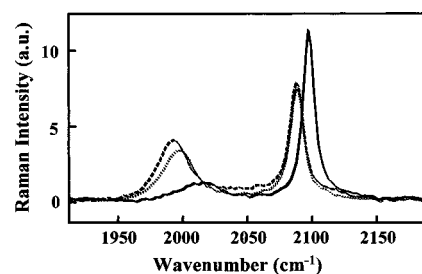
Department of Chemistry, Northwestern University  
Evanston, Illinois 60208

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The charge-transfer resonance Raman spectra of  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$  taken in several solvents show that the Franck–Condon activity of the different CN stretch modes is strongly solvent dependent. These results imply that the choice of solvent can control high-frequency vibrational mode coupling to electron transfer (ET). Specific couplings between solute (donor/acceptor, DA) vibrations and solvent have previously been thought to be important only for the low-frequency modes of the system.

A polar solvent often largely controls the relative free energies of DA and  $\text{D}^+\text{A}^-$  in solution.<sup>1–3</sup> Similarly, intramolecular vibrations of DA and  $\text{D}^+\text{A}^-$  exhibit different equilibrium displacements in DA and  $\text{D}^+\text{A}^-$  and, thus, also contribute to the relative free energies, which is crucial in the Marcus inverted regime.<sup>4–6</sup> A model of the ET mechanism must account for the reorganization energies and dynamics among these modes, and resonance Raman spectra are particularly useful for extracting specific mode coupling information.<sup>7–14</sup>

As shown in Figure 1, we have collected the resonance (1064 nm) Raman spectra of  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$  in three solvents: water ( $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ ), formamide (FA), and *N*-methylformamide (NMF).<sup>15</sup> These data show the CN vibrational stretch region. The mode at ca. 2100  $\text{cm}^{-1}$  has been previously assigned to the bridging CN ligand.<sup>7–9,14</sup> The mode at ca. 2000  $\text{cm}^{-1}$  in NMF and FA is assigned to the stretch of the CN ligand trans to the bridging ligand.<sup>16</sup> A much weaker band, also assigned to the trans



**Figure 1.** Resonance Raman spectra of FeRu in  $\text{D}_2\text{O}$  (solid), formamide (dotted) and *N*-methylformamide (dashed). The bridging CN of  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$  is seen at ca. 2100  $\text{cm}^{-1}$  and scatters strongly in all three solvents. On the other hand, the lower frequency Raman active CN mode is strong and seen at ca. 2000  $\text{cm}^{-1}$ , only in formamide and *N*-methylformamide solvents. In  $\text{D}_2\text{O}$  the band is significantly shifted (2014  $\text{cm}^{-1}$ ) and is very much weaker. The shift and change in Raman activity is attributed to strong solvent–solute interaction at the CN group trans to the bridging ligand.

CN ligand, is seen at 2014  $\text{cm}^{-1}$  in  $\text{D}_2\text{O}$ . The cis CN modes are not Raman observed to any significant extent in any of these three solvents. On the other hand, the IR spectra in this frequency range (data not shown) indicate a strong band at 2050  $\text{cm}^{-1}$ , which may be assigned to the *cis*-CN stretch. The intensity of the *trans*-CN stretch band is strongly solvent dependent, as is its frequency shift.

We have also collected the Raman excitation profile for  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$  in  $\text{D}_2\text{O}$ . The relative Raman intensities of the CN modes at ca. 2000 and 2100  $\text{cm}^{-1}$  do not depend significantly on the excitation frequency (data not shown, see the Supporting Information). These results indicate that the variation of Raman intensities among the three solvents is not a consequence of the wavelength of the exciting radiation relative to the origin of the charge-transfer band.

We have simultaneously fit the resonance Raman and CT absorption spectra.<sup>17,19</sup> A variety of approaches<sup>7,11–14,20–23,25–32</sup> have been used by others to account for solvent broadening of the resonance Raman and charge-transfer absorption bands, to

(17) The following is one functional form that has been used to fit the CT absorption spectrum:  $I(\nu) \propto \sum_{i,j,k} (\lambda_i/\nu_i)^{i!} (\lambda_j/\nu_j)^{j!} (\lambda_k/\nu_k)^{k!} \exp(-\lambda_i/\nu_i) \exp(-\lambda_j/\nu_j) \exp(-\lambda_k/\nu_k) \exp(-\nu - (\lambda_{cl} - \Delta G^\circ + i\nu_1 + j\nu_2 + k\nu_3)^2/4\lambda_{cl}k_bT)$ . Here,  $\lambda_i$  are vibrational reorganization energies,  $\nu_i$  are vibrational frequencies,  $\lambda_{cl}$  is the classical reorganization energy, and  $\Delta G^\circ$  is the minimum free energy difference between the ground and excited electronic states. The variations in Raman intensity among the modes can be related to unitless normal coordinate distortions,  $\Delta$ , and ultimately to the vibrational reorganization energies,  $\lambda_i$ , as outlined by Heller and co-workers.<sup>18</sup> In a particularly simple case, the relationships are  $I_1/I_2 = \omega_1^2 \Delta_1^2 / \omega_2^2 \Delta_2^2$  where  $\omega$  is  $2\pi$  times the vibrational frequency.<sup>18</sup> If the local coordinate approximation is appropriate, the  $\Delta$  value can be converted to absolute bond distortions ( $|\Delta a|$ ) by  $|\Delta a| = (\Delta^2 \nu / \omega b)^{1/2}$  where  $\mu$  is the reduced mass and  $b$  is the effective bond degeneracy. From the normal coordinate or bond distortion data, individual contributions ( $\lambda_i$ ) to the vibrational reorganization energy can be calculated:  $\lambda_i = (1/2)b(\Delta a)^2 f = (1/2) \Delta^2 \nu_i$ . We have also used detailed analysis of the charge-transfer and resonance Raman spectra without assuming the short time behavior, see ref 19. The short time approximation is satisfactory if the absorption band is sufficiently homogeneously broadened and excitation is not postresonance. Such broadening is typical in related systems. See refs 13, 22, and 25.

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(15) Solvents were purchased from Aldrich and used without further purification. The concentration of  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$  is 0.001 M in all three solvents. The measurements are performed using a FT-Raman spectrometer with excitation wavelength of 1064 nm, which comes from a Nd:YAG laser. The laser power for experiments is 350–400 mW. The sample is placed in a 4 mm diameter NMR tube and stirred by a magnetic stirrer to avoid heating of the sample by the Nd:YAG laser.

(16) The change in the molecular orbitals that leads to the frequency upshift of the bridging ligand is also responsible for the downshift in the *trans*-CN ligand.

**Table 1.** Solvent-Dependence of Resonance Raman Bands of  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$ 

solvent <sup>a</sup>	mode	$\nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	$\Delta\nu_{\text{FWHM}}$ ( $\text{cm}^{-1}$ )	band area (relative)	$\lambda_{\text{vib}}$ ( $\text{cm}^{-1}$ )	$ \Delta a $ (Å)
D <sub>2</sub> O	bridge CN	2098(1)	11(1)	1.0	622(20)	0.038(0.001)
D <sub>2</sub> O	<i>trans</i> -CN	2014(1)	38(2)	0.25	162(10)	0.020(0.001)
D <sub>2</sub> O	Fe–C bridge	598(1)	31(3)	0.41	902(30)	0.131(0.001)
FA	bridge CN	2089(1)	13(1)	0.68	453(20)	0.033(0.001)
FA	<i>trans</i> -CN	1996(1)	29(1)	0.61	428(20)	0.034(0.001)
FA	Fe–C bridge	592(2)	31(3)	0.17	408(20)	0.089(0.001)
NMF	bridge CN	2089(1)	13(1)	0.72	505(20)	0.035(0.001)
NMF	<i>trans</i> -CN	1993(1)	29(1)	0.75	550(20)	0.038(0.001)
NMF	Fe–C bridge	592(2)	33(3)	0.28	697(25)	0.116(0.001)

<sup>a</sup> The classical reorganization energies (for solvent and intramolecular modes with frequencies  $< kT$ ) were 4550, 3560, and 3300  $\text{cm}^{-1}$  in D<sub>2</sub>O, formamide, and *N*-methylformamide, respectively. The driving forces were  $-4600$ ,  $-4100$ , and  $-4000$   $\text{cm}^{-1}$  in D<sub>2</sub>O, formamide, and *N*-methylformamide, respectively.

extract the vibrational reorganization energies. We combined the low-frequency modes of the solute and solvent in a single classical degree of freedom. Furthermore, in our analysis the relative displacements of the three modes, two high and one medium vibrational frequency quantal degree of freedom, were fixed by the corresponding ratios of quantal vibrational mode displacements.<sup>24</sup> These relative displacements were calculated both by the short time approximation to resonance Raman intensities and by more detailed time-dependent scattering theory,<sup>19</sup> and the two methods provided similar estimates. The absolute magnitudes of the reorganization energies in the high-frequency modes were obtained from the fit to the charge-transfer absorption band. In this way, the high-frequency reorganization energies are treated consistently with the electronic absorption band energy and width, without requiring detailed knowledge of the origin of band

(24) Resonance Raman bands were fit with Voigt profiles. The bridging CN band is  $>98\%$  Lorentzian in all solvents, the *trans*-CN band is ca. 60% Lorentzian in D<sub>2</sub>O and  $>70\%$  Lorentzian in formamide and *N*-methylformamide. The band areas were referenced to perchlorate ion and the CT absorption spectra. We note that the relative scattering intensity equation in ref 17 assumes that the mode does not change frequency between the two electronic states. Electrochemical studies indicate that the vibrational mode is likely to change by 100  $\text{cm}^{-1}$  with metal oxidation state change, which could lead to as much as 10% increase of the vibrational mode reorganization energies.

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broadening.<sup>17</sup> The results of these fits are summarized in Table 1, and examples may be seen in the Supporting Information.

The solvent dependence of the resonance Raman and infrared spectra most likely reflects solvent electrostatic effects on the ground electronic state wave function of the solute, which is significantly localized on the Fe center.<sup>31,33</sup> The blue-shift in the metal-to-metal charge transfer spectrum with more polar (and protic) solvent and the frequency shift on the low-frequency CN resonance are consistent with solvent perturbation on the Fe side of the dimer. Solvent-induced alterations in solute electronic and nuclear structure may result from strong solute–solvent interactions at the most basic cyanide group, the *trans*-CN.

These resonance Raman spectra also suggest that in this class of binuclear metal systems the solvent determines which vibrational modes couple to the radiationless,<sup>5,13,26–30</sup> electronic ground-state recovery (reverse ET) following optical excitation. Time-resolved optical pump/IR probe experiments to test this prediction are in progress.

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**Supporting Information Available:** Charge-transfer spectra of  $(\text{CN})_5\text{FeCNRu}(\text{NH}_3)_5^-$  in D<sub>2</sub>O, formamide, and *N*-methylformamide, Raman excitation profile in D<sub>2</sub>O, and analysis of charge transfer and resonance Raman spectra with time-dependent scattering theory (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(33) Transition dipole coupling effects between the solute and solvent do not play a significant role because the IR spectra of FeRu in water and deuterated water are nearly indistinguishable.