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Resonance Raman Spectrum Does Not Predict Vibrational State Distributions Caused by Ultrafast Reverse Electron Transfer of $(CN)_5FeCNRu(NH_3)_5$

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Resonance Raman Spectrum Does Not Predict Vibrational State Distributions Caused by Ultrafast Reverse Electron Transfer of $(CN)_5FeCNRu(NH_3)_5^-$

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It is generally thought that the resonance Raman spectrum can be used to predict the vibronic paths of radiationless decay or intramolecular electron transfer (ET) following electronic photoexcitation.[1-5] We show that this assumption does not hold for the $S_1 \rightarrow S_0$ ET of $[(CN)_5 Fe^{III} CN Ru^{II} (NH_3)_5]^-$ in solution following $S_0 \rightarrow S_1$ optical excitation. Instead, vibrational modes that are not observed in the charge transfer resonance Raman spectrum, *i.e.*, are not immediately displaced with photoexcitation of the ground electronic state, are active in the reverse, radiationless ET process.

The metal-metal charge transfer in $[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^-$ can be formally represented as

$$[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^- \underset{\text{reverse ET}}{\overset{h\upsilon}{\rightleftharpoons}} [(CN)_5 Fe^{III} CN Ru^{II} (NH_3)_5]^-$$

Optical excitation of the charge transfer absorption band corresponds to direct ET between the metal centers. This excited electronic state relaxes to the ground electronic state by reverse ET. The theoretical formulation of the thermally and optically induced ET reactions of these bimetallic systems was developed by Marcus,[6] Sutin[7] and Hush,[8] among others. Recent experimental work in resonance Raman[1-4] and time-resolved spectroscopy, at both optical[5,9] and infrared[10,11] frequencies on mixed valence and related ET systems has sought to characterize the roles of vibrations in ET reactions.

Experimental

The apparatus and experimental method have been described in detail elsewhere.[12] Briefly, 100 fs excitation pulses centered at 800 nm are used to photoinduce charge transfer and the

subsequent vibrational dynamics in the ground and excited electronic states are interrogated by femtosecond infrared probe pulses. Time resolved IR spectra and transient kinetic signals are obtained by varying the relative time delay of pump and probe pulses. The transmitted IR pulses are detected using a monochromator and a HgCdTe photodiode array. For transient absorbance measurements, sample solution is placed in a 0.75 mm pathlength spinning cell with thin CaF_2 windows, which provides a fresh sample volume for every laser shot. The pump energy is 5 μJ/pulse and is focused to 0.300 mm. A half-wave plate is placed in the pump beam to allow polarization-dependent measurements. The concentration of $[(CN)_5\ Fe^{II}\ CN\ Ru^{III}\ (NH_3)_5]^-$ in formamide (FA) solvent was 7 mM.

Results and discussion

The charge transfer band of FeRu in FA is found in the near infrared wavelength region, with maximum intensity at 1.2 μm. This is the transition that is induced by the optical pulse of the laser. The charge transfer band shape has been fit previously[4] using the resonance Raman data and a classical model for the solvent and low frequency vibrations of the solute.

Figure 1 shows the static infrared and 1.06 μm resonance Raman spectra of FeRu in FA.[13] These spectra show three bands assigned to the trans, cis, and bridging CN modes at 1998, 2051, and 2089 cm^{-1}, respectively. Here trans and cis mean trans and cis to the bridging CN. Note that the cis band is present in the IR spectrum, but not in the resonance Raman spectrum. These resonance Raman spectra illustrate the bridging and trans CN modes that are predicted to be excited in the electron transfer reaction.[2,4,5] The IR probe pulse detects equilibrium and non-equilibrium CN vibrational absorbances.

Figure 2 shows the transient infrared difference spectra of FeRu/FA in CN stretch region, where the signal shows the changes in the sample vibrational spectrum caused by the pump pulses which change the sample's electronic state. Negative ΔOD features correspond to loss of ground state vibrational absorptions and positive ΔOD features correspond to new vibrational absorptions created as a result of excitation by the optical pump pulse. There are bleaches of ground electronic state vibrational absorbances at *ca* 2000 cm^{-1} and 2050 cm^{-1}, which correspond to trans CN and cis CN stretches, respectively, as determined by anisotropy measurements.[14] Fits of a convolution of the excitation and probe pulses with a single exponential form for the sample response gives ca 200 fs relaxation times for the reverse electron transfer, consistent with earlier optical measurements.[5] This means that most of the spectral dynamics shown in Figure 2 are due to relaxation of non-equilibrium vibrational absorptions of the ground electronic state, which follow reverse electron transfer.

One of the most important features of Figure 2 is the differential absorbance peak at 2030 cm^{-1}. The anharmonicity of the CN mode is ca 20 cm^{-1}.[15] Therefore, this feature at 2030 cm^{-1} reflects $v = 1 \rightarrow v = 2$ transitions of the cis CN mode.[16] Similarly, the differential absorbance peak at 1985 cm^{-1} reflects excited vibrational state absorption of the trans CN mode in S_0. Static heating solutions of $[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^-$ in formamide shows that the cross section of the bridging CN stretch increases intensity with heating, and we explain the differential absorption at 2080 cm^{-1} as caused by rapid local heating as a consequence of energy release by the radiationless decay process. The frequencies of the ground state vibrational absorbances shift less than 1 cm^{-1} with bulk thermal heating from 16 to 34 °C. Our transient IR data are thus consistent with ca 20% population of the v = 1 level of the cis and trans vibrational modes following reverse electron

transfer. The kinetics at 2030 and 1980 cm^{-1} indicate that the T_1 times for the cis and trans modes are *ca* 10 ± 3 ps and 5 ± 3 ps, respectively.

The resonance Raman spectra show no activity in the cis-CN mode, and thus the transient infrared evidence of excitation in this mode is unexpected. We now consider whether this cis-CN vibrational excitation is caused by ultrafast electron transfer or by vibrational energy redistribution[17,18] within one electronic state. Vibrational energy redistribution within the ground electronic state (Fe(II)Ru(III)) is too slow to account for the ca 100-200 fs appearance of energy in cis-CN, based on the 20 cm^{-1} vibrational linewidths that set a conservative bound on the vibrational state lifetime of ~ 500 fs. The short excited state (Fe(III)Ru(II)) lifetime causes the CN resonances to be broad (50-100 cm^{-1}) and overlapping, and thus provide little information on cis- to trans-CN vibrational energy exchange in that excited state. However, we note (1) that the vibrational resonances of the electrochemically prepared species Fe(III) $(CN)_6^{3-}$ are less than 20 cm^{-1} wide, and (2) that the anisotropy shows that the cis-CN mode is perpendicular to trans- and bridging-CN modes which could potentially donate energy, thus mechanical coupling is likely to be weak. We have also changed solvents (formamide to deuterated water) to alter the phonon spectrum of the sample at 50 cm^{-1} and find similar vibrational excitation of cis-CN. Sub-100 fs vibrational energy redistribution in S_1 is therefore unlikely and we conclude that the population of the cis-CN excited vibrational states is caused by electron transfer.

We can explain our results in the following way. If the vibrational modes coupled to the reverse electron transfer are not modes that are Franck-Condon active in the equilibrium configuration of the ground electronic state, then relaxation within the excited electronic state leads to a new set of modes that vibronically couple in the return to the ground electronic state.

Such effects have not been previously observed in this class of molecules or in electron transfer systems in general, although related effects have been observed in smaller systems.[20, 21] The data presented here therefore suggest that charge transfer absorption or resonance Raman spectra may not always provide the inner sphere (vibrational) reorganization information necessary to characterize the radiationless electron transfer process.

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13. Solvents were purchased from Aldrich and used without further purification. For static IR absorption and resonance Raman measurements, the concentrations of FeRu were 0.001 M in formamide(FA). The path length was 0.1 mm for static IR absorption measurements. The measurements were performed using FTIR and FT-Raman spectrometer. For Raman measurements, the excitation wavelength was 1064 nm, which came from a Nd:YAG laser and the power for experiment was 350 - 400 mW. The sample was placed in 4 mm diameter NMR tube and stirred by a magnetic stirrer to avoid heating of the sample by the Nd:YAG laser light.

14. The anisotropies measured at 1998 and 2051 cm^{-1} were 0.35 ± 0.03 and -0.2 ± 0.03, respectively, at 0 ps. The anisotropy is calculated according to the equation $r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ correspond to absorbance change with the pump and probe electric fields parallel and perpendicular, respectively. Employing the second order Legendre polynomial, where $r = 0.2\,(3\cos^2\theta - 1)$, the values of anisotropy measured indicate that the resonances at 1998 corresponds to a mode that is approximately parallel with the charge transfer transition moment. The band at 2051 cm^{-1} corresponds to a mode which is approximately perpendicular to the charge transfer absorption transition moment. In conjunction with the characteristic frequencies,[1] these results lead to our assignment of these resonances at 1998 and 2051 cm^{-1} to the trans and cis modes, respectively.

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Figure Captions:

Figure 1. Static infrared (solid line) and resonance Raman (dashed line) spectra of $[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^-$ in formamide solvent. Three resonances are observed, at 1998, 2051, and 2089 cm^{-1}. These three resonances are assigned to trans-CN, cis-CN and bridging CN. The 1998 band is strong in both the IR and resonance Raman spectra, while the 2089 band is strong only in the resonance Raman spectrum and the 2051 cm^{-1} band is strong only in the IR spectrum. The resonance Raman bands are commonly used to predict the radiationless decay mechanism (reverse electron transfer), thus a simple model would predict that there should be no vibrational excitation of the cs-CN modes as a consequence of electron transfer.

Figure 2. The infared transient differential absorption spectra (photoexcited sample spectrum minus unexcited sample spectrum) of $[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^-$ in formamide following charge transfer excitation using 100 fs, 800nm pump and probe pulses. Each line corresponds to a different delay time between pump and probe, as indicated in the legend. The inset shows spectral dynamics at 2030 cm^{-1} (upper black line), 2004 cm^{-1} (middle red line), 2049 cm^{-1} (lower blue line). The charge transfer excited state relaxes within ca 200 fs following preparation, and most of the observed spectral dynamics correspond to evolution within the ground electronic state. The bleach (neg ΔOD) signal at 1998 and 2051 cm^{-1} correspond to loss of ground vibrational state (the $v = 0$ level) absorbances of the trans- and cis- CN stretch modes of $[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^-$. The positive ΔOD features found to slightly lower frequencies of each bleach, at 1980 and 2030 cm^{-1} correspond to excited vibrational state transitions ($v = 1 \rightarrow v = 2$) of the trans- and cis- CN modes of $[(CN)_5 Fe^{II} CN Ru^{III} (NH_3)_5]^-$, where the frequency shift is due to

vibrational anharmonicity. The presence of non-equilibrium vibrational states of the cis-CN mode would not be predicted by conventional theories of electron transfer and radiationless decay using the spectra seen in Figure 1.

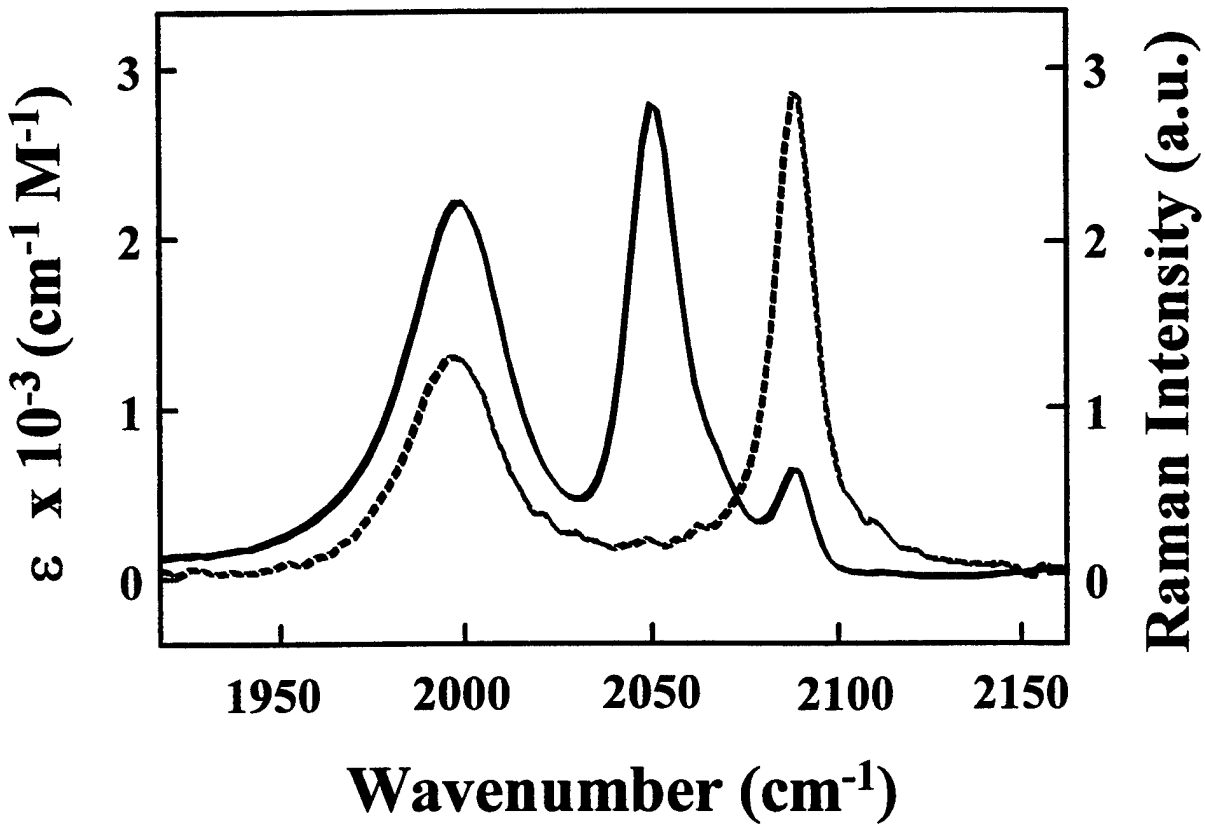

Fig. 1 (Wang & Walker)

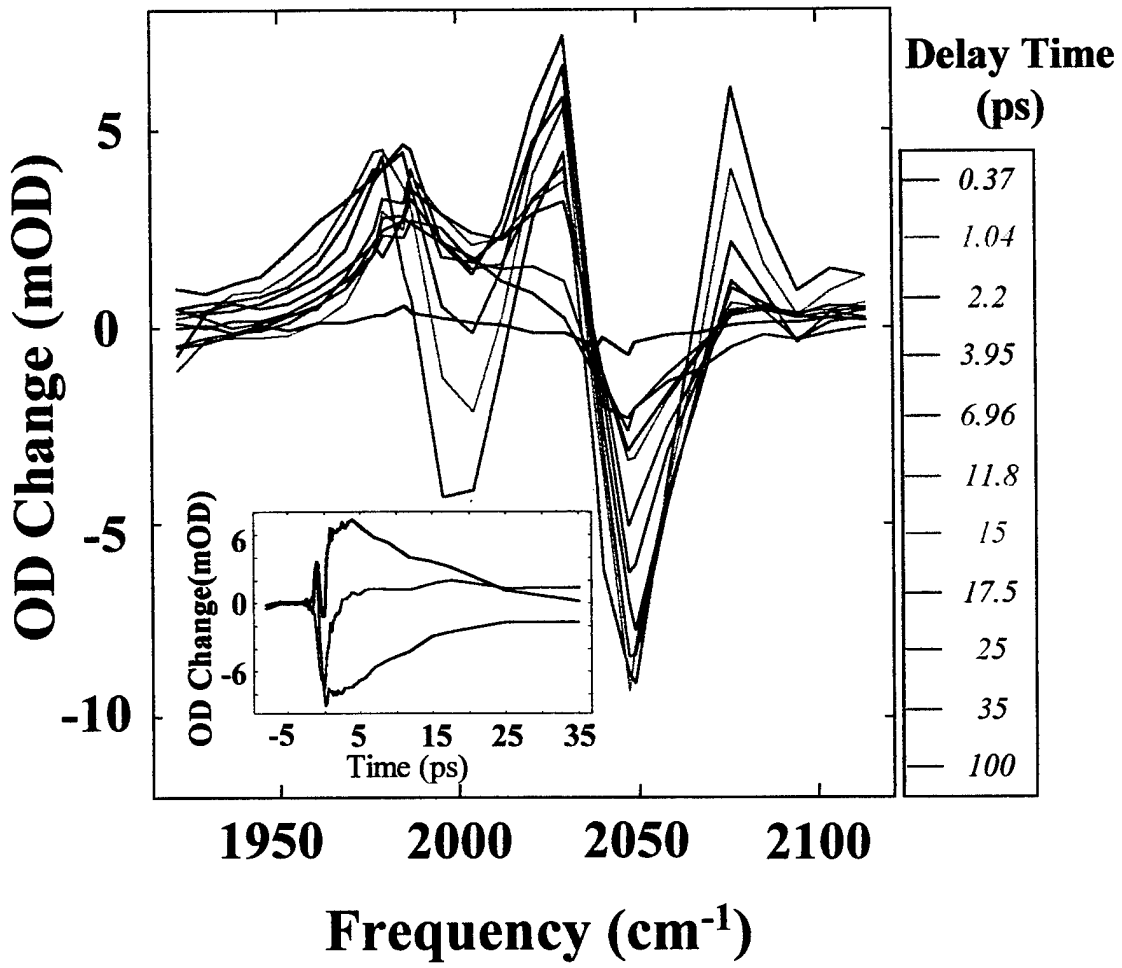

Fig. 2 (Wang & Walker)

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It is generally thought that the resonance Raman spectrum can be used to predict the vibronic paths of radiationless decay or intramolecular electron transfer (ET) following electronic photoexcitation. We show that this assumption does not hold for the $S_1 \rightarrow S_0$ ET of $[(CN)_5 Fe^{III} CN Ru^{II} (NH_3)_5]^-$ in solution following $S_0 \rightarrow S_1$ optical excitation. Instead, vibrational modes that are not observed in the charge transfer resonance Raman spectrum, *i.e.*, are not immediately displaced with photoexcitation of the ground electronic state, are active in the reverse, radiationless ET process.

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