#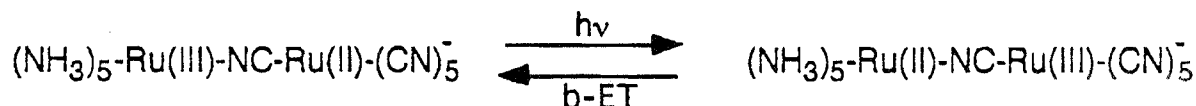 Direct Measurement of the Nuclear and Solvent Contributions to the Electron-Transfer Dynamics in Mixed Valence Metal Dimers

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The electron-transfer in mixed valence metal dimers is investigated with sufficient time resolution (20 fs) to unravel coherent and incoherent electronic, vibrational, and solvent motion for the first time. These compounds represent an ideal class of reactions on which to develop condensed-phase electron-transfer (ET) theories.[1, 2] An example in these reactions is the ruthenium-ruthenium mixed valence compound (RuRu):

$$(NH_3)_5\text{-Ru(III)-NC-Ru(II)-(CN)}_5^- \underset{\text{b-ET}}{\overset{h\nu}{\rightleftharpoons}} (NH_3)_5\text{-Ru(II)-NC-Ru(III)-(CN)}_5^-$$

Photoexcitation initiates the migration of an electron between metal centers with internal conversion from the excited state to the ground state corresponding to the back-electron transfer. We have constructed a 20-fs absorption spectrometer based on a Ti:Sapphire oscillator which is capable of measuring the ultrafast reaction dynamics.[3]

This work represents the first direct measurement of the electron-transfer time of RuRu in water allowing for the investigation of both nuclear and solvent motion in the reaction dynamics.

The transient pump-probe signal for RuRu in H_2O is shown in Figure 1A. The largest component of the response is the symmetric, coherence coupling signal centered at zero time. Closer evaluation of the transient (Figure 1B) reveals the presence of the ground-state bleach that evolves into an absorption with the decay of this feature completing the dynamics. Kinetic analysis of this transient reveals that the coherence coupling signal follows the instrument response. The ground-state bleach recovers with a time-constant of 85 ± 10 fs. The ground-state absorption corresponding to excess energy in vibrational and/or solvent degrees of freedom decays in 880 ± 160 fs.

The coherent nuclear response of RuRu is observed in residual difference between the fit and the transient (Figure 1B). Figure 2 presents the Fourier transform of the residual. The frequencies determined from this analysis agree with those observed in the post-resonance Raman spectrum demonstrating that this response originates from the solute. This observation combined with the absence of an excited-state absorption in this spectral region indicates that the oscillatory response is due to a displaced ground-state population created by impulsive-stimulated Raman scattering (ISRS).[4] The residual was also modeled with three components with frequencies at 170, 280 and 480 cm^{-1} and separate dephasing times. An average vibrational dephasing time of ~300 fs was determined in agreement with the Raman linewidths.[5]

Excitation perpendicular to the probe polarization results in a dramatic reduction in the amplitude of the coherence coupling signal relative to ground-state bleach and absorption due to anisotropy differences between these features (Figure 1C).[6] The kinetics observed for perpendicular excitation were in agreement with the parallel data demonstrating that we have accurately measured the electron-transfer dynamics.
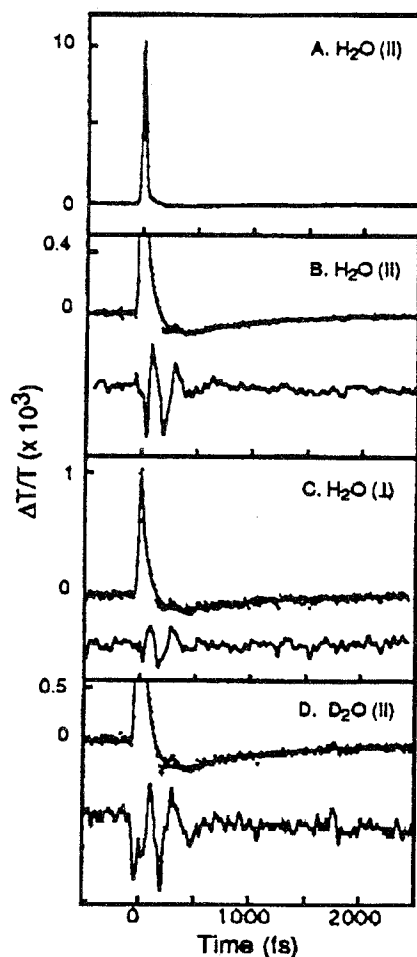
Figure 1. A. Transient absorption of RuRu in H_2O. B. Expansion of A with residual difference between the data and fit at the bottom. C. Transient for perpendicular pump and probe polarizations. D. RuRu in D_2O.
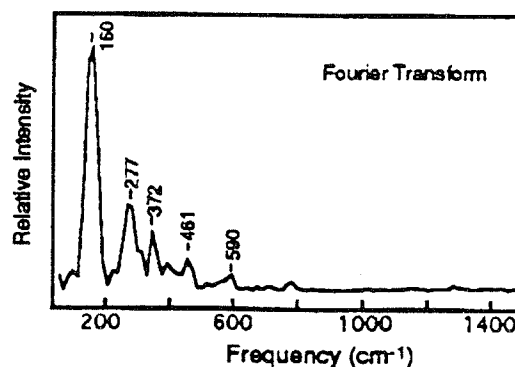

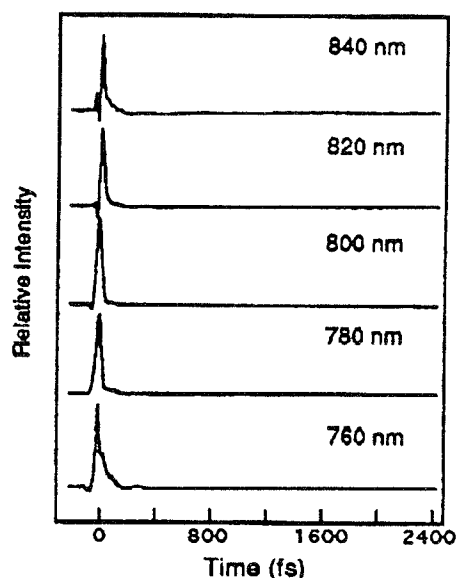**Figure 2.** Fourier transform of residual in Fig. 1B.

Figure 3. Dynamic absorption spectra of RuRu in H_2O.

Figure 1D presents the pump-probe transient obtained for RuRu in D_2O. Although the transient appears similar to that obtained in H_2O, anlaysis of the ground-state dynamics reveals that the time-constant for bleach recovery increases to 122 ± 20 fsec. The ground-state absorption decays in 800 ± 240 fsec similar to the H_2O dynamics. To ascertain the role of hydrogen solvent/ligand exchange on the kinetics in D_2O, the dynamics at pH 3 were also investigated. At this lower pH, the exchange half-life is 8 hours providing ample time to measure the kinetics in the absence of this process.[7] The kinetics determined from this study were in agreement with the pH 7 results demonstrating that the rate reduction in D_2O is due to the solvent.

The data presented here provide a detailed picture of RuRu electron-transfer dynamics:

Rapid electronic dephasing. The symmetric shape of the coherence coupling signal and the observation that the signal follows the instrument response indicates that electronic dephasing is rapid. Also, the amplitude of this signal relative to the ground-state bleach was insensitive to a 2-fold increase in pulse width unlike the behavior observed in other systems in which the electronic dephasing and pulse width are comparable.[8] This observation establishes that the electronic

dephasing time is ≤20 fs.[9]   Analysis of the ground-state electronic absorption band has demonstrated that the solvent contribution to the reorganization energy is 3700 cm^{-1} consistent with large coupling between the solvent and the electronic transition.[10] This interaction results in rapid electronic dephasing providing for an electronically incoherent back-electron transfer.

Electron-transfer is faster than vibrational dephasing. Decay of the oscillatory nuclear response demonstrates that ground-state vibrational dephasing occurs in ~300 fsec. If we project a similar dephasing time in the excited state, the electron transfer would occur before vibrational dephasing. This is in agreement with measurements of ground-state vibrational energy deposition in excess of that expected if vibrational relaxation of the excited state were complete.[11] However, the electron-transfer times measured here are similar to estimates from previous absorption experiments in which coherent excitation of vibrational modes was not possible. [10, 12] Therefore, the rapidity of the back-electron transfer is most likely the result of strong electronic coupling and not due to the existence of vibrational coherence.

Solvent hydrogenic motions are coupled to the back-electron transfer. The back-electron transfer rate reduction between H_2O and D_2O demonstrates that solvent hydrogenic motions are involved in the reaction dynamics. Molecular dynamics simulations on similar systems have suggested that librational motions of the first solvent shell participate in the electron transfer.[13] This study provides direct experimental evidence for this hypothesis. Also, the observation of specific solvent vibrational motions participating in the reaction dynamics illustrates the limitation of dielectric continuum based electron-transfer theories to model the quantum aspects of solvation.

Mixed valence metal dimers are ideal for the development of electron-transfer theories. In Figure 3, we present the dynamic absorption spectra of RuRu obtained throughout the probe spectral profile. The spectral trends are as expected with the coherence term largest at the pump-probe frequency, a larger absorption signal on the red-edge of the ground-state absorption band and an oscillatory response which is phase shifted between 840 and 760 nm consistent with ISRS. The results presented here in combination with the previous static and transient absorption and resonance Raman data establishes a unique opportunity to develop and test theoretical descriptions of electron transfer. Accurate modeling of these data is currently underway to develop a complete picture of RuRu reaction dynamics.

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