

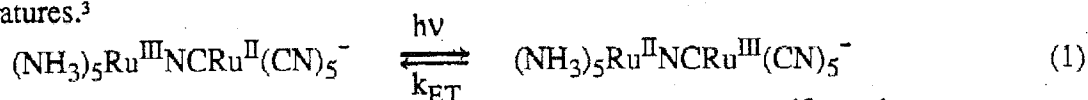
Ultrafast Studies on Intervalence Charge Transfer^a

K. Tominaga, D.A.V. Kliner,^b J. T. Hupp,^c and P.F. Barbara

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455 USA

Mixed-valence metal complexes have played a central role in the development of the theory of electron-transfer (ET) reactions.¹ These compounds contain two metal atoms in different oxidation states, typically +2 and +3. An absorption band is often observed in the near IR or visible, corresponding to the transfer of an electron between the two metal centers, i.e. intervalence absorption. Much theoretical work has addressed the connection between this photoinduced charge transfer and the analogous thermal ET reaction. Recently, the first direct ultrafast measurements were reported for an intervalence absorption.²

In this paper we report the femtosecond transient-absorption spectra for the following metal/metal intervalence photoinduced charge-transfer reaction in a broad range of solvents and temperatures.³



The observed electron-transfer rates (k_{ET}) fall in the range of $\sim 10^{12} \text{ sec}^{-1}$ to greater than 10^{13} sec^{-1} . The critical role played by intramolecular vibrational modes in promoting the ET reaction is demonstrated by the relative insensitivity of k_{ET} to the solvent and temperature and by the fact that, in many instances, k_{ET} exceeds $1/\tau_s$ (where τ_s is the time scale for diffusive solvent motion), which is in marked contrast to several recently reported fast ET reactions.⁴

The kinetics have been analyzed using various theoretical descriptions available from the literature¹ to reveal a surprisingly complex interaction of intramolecular and intermolecular modes in these ET reactions. Especially noteworthy is the wealth of spectroscopic data available for these mixed-valence compounds. In particular, resonance Raman and static absorption spectra of the metal-metal charge-transfer transition provide frequencies and displacements (reorganization energies) of the vibrational modes coupled to the ET reaction.⁵ These molecular parameters have been used to evaluate multi-mode expressions for the reaction rate. The ET rates are calculated by employing the current ET theories with assumption of the separation of the solvent motion, a fast dissipative ($< 50 \text{ fs}$) and a slow diffusive ($\sim 0.5 \text{ ps}$) motions. The predicted values for $1/k_{\text{ET}}$ range from 25 to 160 fs, depending on the fraction of the reorganization energy of the fast solvent motion. This shows a good agreement with the measured ET rates. This analysis elucidates the important pathways for electron transfer and allows a quantitative evaluation of the theoretical treatments to be performed.

The transient pump-probe apparatus has been described in previous publications.⁶ Two ultrafast spectrometers were used, one for single-wavelength measurements ($\lambda_{\text{pump}} = \lambda_{\text{probe}}$) and one for measurements in which λ_{pump} and λ_{probe} were different. The temperature of the sample could be varied between -100° and 70° C .

Figure 1 shows transients recorded for Reaction (1) in H_2O and NMF at 20° C and glycerol at -100° C . The transients were fit to a sum of exponentials and can generally be characterized by two time scales (Table 1): 1) A pulse-limited ($< 0.1 \text{ ps}$) transient bleach (except glycerol, see below), and 2) A slower bleach or increased absorption with a decay time that depends on the solvent and an amplitude that is 5-20% of the fast component. Similar results were obtained for other intervalence ET reactions that we have investigated.

The dominant fast response is ascribed to electron transfer. For many of the solvents and temperatures investigated, the ET time ($1/k_{\text{ET}}$) is $< 0.1 \text{ ps}$ (see Table 1) despite large variations in τ_s . In glycerol, however, the ET rate for Reaction (1) is not pulse limited and is sensitive to temperature and to deuteration of the solvent OH groups. The ET time in glycerol varies from 0.27 ps at 50° C to 0.74 ps at -100° C . A pronounced, temperature-dependent isotope effect is observed: $k_{\text{ET}}(\text{glycerol})/k_{\text{ET}}(\text{glycerol-}d_3) = 1.2$ at 20° C and 1.5 at -100° C . Thus, high-frequency solvent fluctuations are clearly coupled to the ET reaction, with H-atom motion involved in the relevant solvent modes. Such modes may include librational or inertial motions.

The behavior of the slower component depends on the relative wavelengths of the analyzing light and the peak of the absorption spectrum. Solvent- and temperature-dependent shifts of the absorption spectrum and the use of both one- and two-color measurements allowed the probe pulse to interrogate different regions of the absorption band. The slower component is tentatively attributed to local heating or ground-state solvation, i.e., to nuclear motions in the solute and solvent. This interpretation is consistent with the measured temperature- and solvent-dependence of the static absorption spectrum.

Table 1
Biexponential Fits to Kinetic Data for Reaction (1)^a

Solvent	T/°C	τ_1/ps^b (A_1)	τ_2/ps (A_2)
H ₂ O	0	≤ 0.1 (0.88)	1.6 (-0.12)
	20	≤ 0.1 (0.89)	1.5 (-0.11)
NMF	0	≤ 0.1 (0.72)	0.5 (0.28)
	20	≤ 0.1 (0.86)	0.9 (0.14)
formamide	0	≤ 0.1 (0.85)	0.6 (0.15)
	20	≤ 0.1 (0.90)	0.7 (0.10)
ethylene glycol	20	0.3 (0.96)	>5 (0.04)
glycerol	70	≤ 0.1 (0.72)	0.4 (0.28)
	-100	0.74 (1.00)	---
	-5	0.43 (0.90)	~6 (-0.10)
	20	0.33 (0.95)	~5 (-0.05)
glycerol-d ₃	50	0.27 (0.97)	~5 (-0.03)
	-100	1.3 (1.00)	---
glycerol-d ₃	20	0.40 (0.95)	~5 (-0.05)

a. Transients were fit to $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$.

Uncertainties in τ_1 and τ_2 are typically ± 10 -15%.

Positive (negative) values of A_1 and A_2 refer to a bleach (increased absorption). For glycerol and glycerol-d₃, the fit is improved by inclusion of a small pulse-limited component, which is attributed to a coherent artifact.

b. τ_1 is identified with electron transfer, i.e., $k_{\text{ET}} = 1/\tau_1$.

References

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- c. Department of Chemistry, Northwestern University, Evanston, Illinois 60208.
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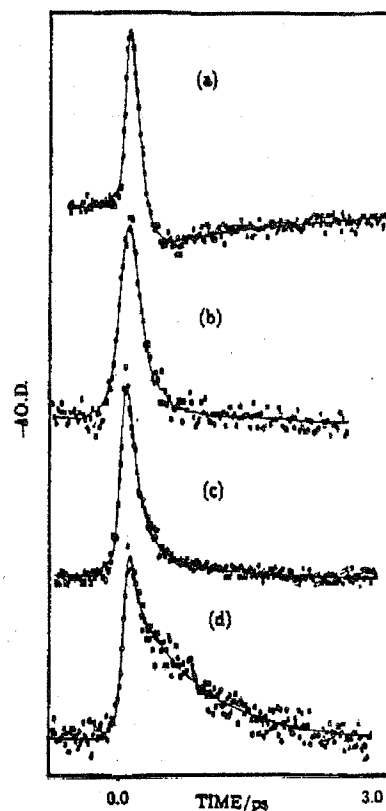


Figure 1. Change in absorption as a function of time delay between the pump and probe pulses for Reaction (1) in H₂O at 20°C ((a) and (b)), NMF at 20°C (c), and glycerol at -100°C (d). The pulse width was 70 fs and $\lambda_{\text{pump}} = \lambda_{\text{probe}} = 792$ nm for (a), (c), and (d), and $\lambda_{\text{pump}} = 800$ nm and $\lambda_{\text{probe}} = 700$ nm for (b).

Positive signal indicates a bleach. The points are the experimental data, and solid curves show biexponential fits to the data.