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Ultrafast Experiments on the Role of Vibrational Modes in Electron Transfer

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Ultrafast Experiments on the Role of Vibrational Modes in Electron Transfer

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The role of vibrational modes in ultrafast photoinduced intramolecular electron transfer reactions is explored. Femtosecond resolved experiments on two chemical classes will be described, namely, metal-metal intervalence electron transfer in mixed valence compounds and intramolecular charge recombination/separation in organic donor/acceptor compound class, the betaines. The results have been analyzed to reveal the complex interactions of intramolecular and intermolecular modes in electron transfer reactions.

A-1

I.   Introduction

The study of charge transfer processes, and in particular homogeneous electron transfer (ET) in solution, is at the forefront of the study of the molecular details of chemical reactions in liquids. The last decade has brought progress to many central problems in ET research, including the role of the solvent in these reactions, the involvement of vibrational degrees of freedom, the role of nuclear tunneling of the solvent and solute (and related quantum mechanical effects), the pathway and "mechanism" of electronic interactions, including long range ET, and other aspects of biological and heterogeneous ET. Recent reviews of the foundations of ET theories have been given by Newton and Sutin[1] and Marcus and Sutin.[2] Theories of ET reactions in solution are formulated in terms of a model in which the transferring electron is *localized* at a *donor* molecular site in the *reactant* and at a different *acceptor* molecular site in the *product*.

Figure 1A portrays the usual curves for an ET reaction with no nuclear degrees of freedom other than the solvent coordinate. The coupling of the solvent coordinate to the ET is quantified by λ, the solvent reorganization energy. ΔG^o is the reaction free energy (driving force) for the ET. A central expression in ET theory due to Marcus is as follows

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^o)^2}{4\lambda}$$

where $\Delta G^{\ddagger}$ is the activation energy for the ET reaction.

As ΔG^o is varied from a very positive value (endothermic ET) the activation energy decreases until $\lambda = -\Delta G^o$ for which $\Delta G^{\ddagger}$ is zero! As ΔG^o is made even more negative, $\Delta G^{\ddagger}$ increases, and correspondingly, k_{ET}, the ET rate decreases. This latter situation, denoted by the inverted regime, is portrayed in Figure 1B.

Vibrational modes in ET theory have been treated classically, quantum mechanically, or both. Figure 1C portrays an ET reaction in the inverted regime for a model system with a single high frequency vibrational mode. The ET occurs most rapidly at the curve crossings (circled regions in Figure 1C). For models with high frequency modes such as Figure 1C, there are multiple *vibronic* crossings.

The basic formulation of thermal ET theory establishes a *connection between spectroscopy and kinetics. Optical charge transfer spectra* can be used to determine many, and in some cases all, of the required parameters to predict k_{ET} using thermal ET theory. The use of the integrated oscillator strength of a charge transfer band to determine V_{el}, the electron coupling matrix element, was pioneered by Hush[3]. Hupp and coworkers have established the use of resonance Raman spectroscopy of charge transfer bands as a powerful tool to determine vibrational parameters for ET reactions[4].
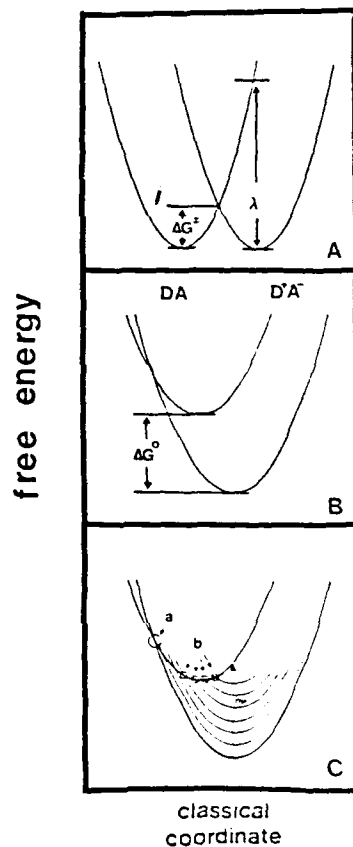
Recent ET theory has focused on the *dynamic solvent effect*, which is the kinetic consequence of noninstantaneous adjustment of the solvent coordinate and solvent molecular orientation to the ET, as discussed in recent reviews[5-11]. The qualitative result of this work is that under certain conditions k_{ET} is predicted to be a function of the relaxation dynamics of the solvent, not just the quasi-equilibrium solvent properties.

This paper describes experiments on two intramolecular charge transfer examples, intervalence metal-metal charge transfer in mixed valence compounds and intramolecular charge transfer in the betaines. The major goal of this work is to explore the interplay of vibrational modes and the dynamic solvent effect in ET kinetics.

Figure 1. Surfaces representing the localization of the transferring electron donor (DA) and acceptor (D⁺A⁻). The classical reorganization energy is λ, the reaction free energy is ΔG^o, the classical barrier to the reaction is $\Delta G^{\ddagger}$. A) $\Delta G^o = 0$. B) $\Delta G^o + \lambda < 0$. C) same as B) with quantized vibrational mode in D⁺A⁻.
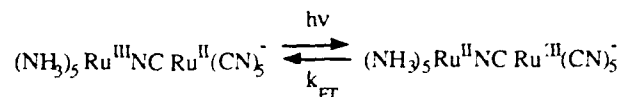
II. Ultrafast Studies on Intervalence Charge Transfer

Mixed-valence metal complexes have played a central role in the development of the theory of ET reactions.[2,3,11] 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. Much theoretical work has addressed the connection between this photoinduced charge transfer and the analogous thermal ET reaction.

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

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

The observed ET rates, k_{ET}, fall in the range of $\sim 10^{12}$ 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.[5,7]

The kinetics have been analyzed using various theoretical descriptions available from the literature[2,3,11] 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.[12] These molecular parameters have been used to evaluate multimode expressions for the reaction rate *with no adjustable parameters.* In general, we find good agreement between the calculated and measured ET rates. This analysis elucidates the important pathways for ET and allows a quantitative evaluation of the theoretical treatments to be performed.

The transient pump-probe apparatus has been described in previous publications.[13] Two ultrafast spectrometers were used, one for single-wavelength measurements ($\lambda_{pump} = \lambda_{probe}$) 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 2 shows absorption transients recorded for the reaction above in H_2O and NMF at 20° C and in glycerol at -100° C for $\lambda_{pump}=\lambda_{probe}=792$nm. The transients were fit to a sum of exponentials and can generally be characterized by two time scales (Table 1): i) A pulse-limited (<0.1 ps) transient bleach (except glycerol, see below), and ii) 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 ($1/k_{ET}$) is <0.1 ps (see Table 1) despite large variations in τ_s. In glycerol, however, the ET rate for the reaction 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: $k_{ET}(glycerol)/k_{ET}(glycerol-d_3)$ = 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 depended 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_2O	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	20	0.3 (0.96)	>5 (0.04)
glycol	70	≤0.1 (0.72)	0.4 (0.28)
glycerol	-100	0.74 (1.00)	---
	-5	0.43 (0.90)	~6 (-0.10)
	20	0.33 (0.95)	~5 (-0.05)
	50	0.27 (0.97)	~5 (-0.03)
glycerol-d_3	-100	1.3 (1.00)	---
	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-d_3, 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., $k_{ET} = 1/\tau_1$.
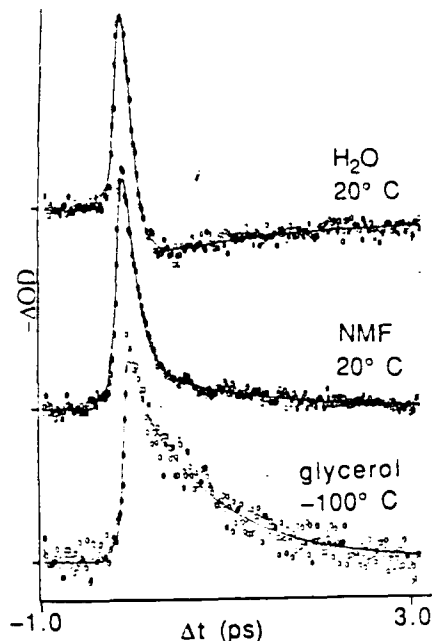
Figure 2. Absorption transients for metal-metal ET in three solvents. Positive signal indicates a transient bleach. Points are the experimental data; solid lines show biexponential fits to the data.

III. The Betaines

We have studied the direct photoinduced ET of betaine-30 and related molecules by femtosecond pump-probe spectroscopy in the visible and near infrared.
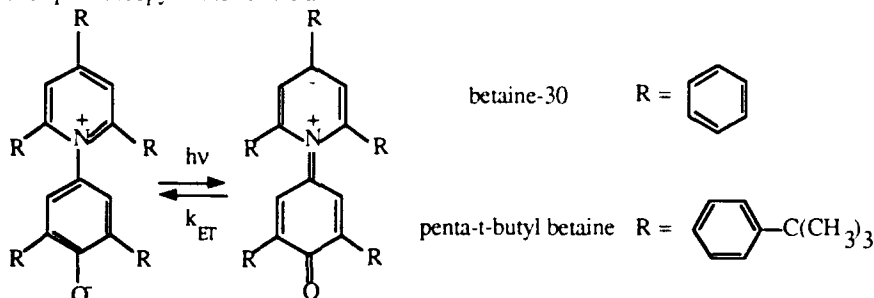

The absorption spectrum of betaine corresponds to direct photoinduced ET and is extremely sensitive to solvent polarity. The ET dynamics have been measured in broad range of solvents, over a large temperature range, in liquid and solid state solutions using ultrafast pump-probe spectroscopy. Representative absorption transients for betaine-30 are shown in Fig. 3. The data have been analyzed to extract the time scales for thermal ET (DA → D⁺A⁻) and for vibrational cooling that occurs after the thermal ET process.[14,15]

Here we emphasize new unpublished variable wavelength pump-probe data on this system.

This new data allows for a detailed analysis of the evolution of the spectral band shape during the ET process. We have made ultrafast time resolved pump-probe measurements with 700nm and 800nm excitation and 640, 700, and 800nm probe wavelengths. The measured dynamics do not appear to depend strongly on the *excitation* wavelength. However, we have observed different ET dynamics and a second dynamical component for some *probe* wavelengths. The second component varies as a function of the probe wavelength. This effect is easily seen in Fig. 4, which displays absorption transients for betaine-30 in acetone. When we probe near the peak of the absorption band at 700nm, Fig. 4b, we are least sensitive to band shifting effects due to local heating hence the measured dynamics should most accurately reflect the reverse ET. However, at a wavelength longer than the absorption peak, 800nm, Fig. 4c, we observe fast recovery of the ground state followed by an increased absorption which decays more slowly than the initial bleach. At a wavelength shorter than the absorption peak, 640nm, Fig 4a, multiexponential dynamics are apparent with the second time scale similar to that observed for the increased absorption at 800nm. We interpret this as evidence of local heating of the betaine molecule environment. Because the betaine absorption band is a strong function of temperature, the absorption band would be expected to shift its peak to longer wavelength with increasing temperature. The reverse ET deposits a large amount of energy into the molecule's environment thereby raising the effective local temperature. This effect would manifest itself in the measured dynamics as an increased absorption on the red edge of the spectrum and an additional bleach on the blue edge, which is what we observe. The recovery of the increased absorption and the additional bleach then correspond to local cooling of the molecule's environment.
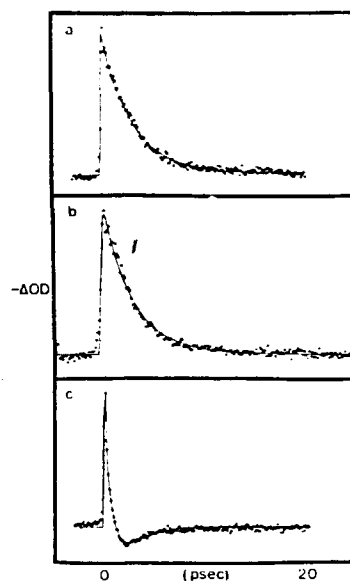
Figure 3. Absorption transients for betaine30 in a) toluene, b) benzene and c) acetone. Points are data, lines are biexponential fits to the data.
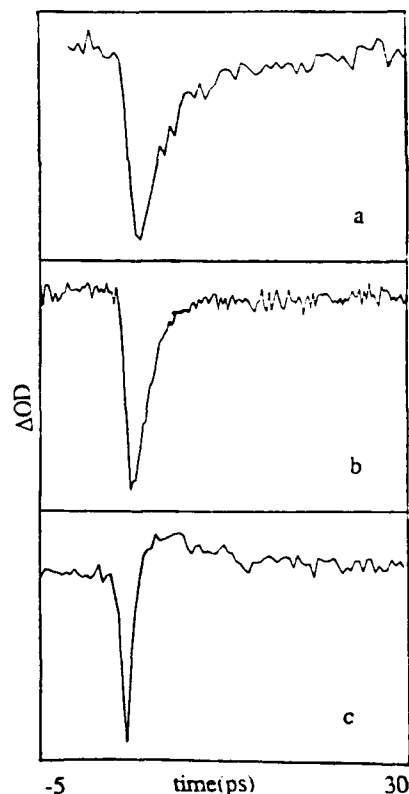
Figure 4. Absorption transients for betaine30 in acetone; $\lambda_{pump}=800nm$, $\lambda_{probe}=$ a) 800nm, b) 700nm and c) 640nm

A theoretical analysis of the results clearly demonstrates that various simple ET theoretical models found in the literature predict rates that are many orders-of-magnitude too slow when compared to experimental results for the betaines.[16,17] The failure of these models stems from the approximate means by which they describe nuclear degrees of freedom of the solute/solvent system. We have developed a new theoretical model[18] that is an extension of an approach by Sumi and Marcus.[16] The simulations from this model are in semiquantitative agreement with various aspects of the time dependent spectroscopy of the betaines. The combined theoretical/experimental results have several general implications toward the understanding of ultrafast ET reactions, including natural photosynthetic systems.

Most of the parameters required for the kinetic predictions can be obtained in a straight forward fashion by fitting the static absorption spectra of the charge transfer band. The results demonstrate that an accurate model for the inverted regime ET in solution minimally requires the following three nuclear degrees of freedom: (i) a solvent mode with a frictional response, (ii) an intramolecular low frequency, classical mode, and (iii) a higher frequency quantized intramolecular mode. Furthermore, the analysis allows for a detailed understanding of the combined effects of solvation dynamics and vibrational excitation in ultrafast ET kinetics.

Acknowledgments:

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