Solvent Control of Electron Transfer Dynamics

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Abstract. We investigate the charge-transfer-to-solvent (CTTS) dynamics of sodide in several solvents. Since this CTTS system has only electronic degrees of freedom, the dynamics provide a window into how solvent motions control electron transfer.

It is of great interest to understand how motions of solvent molecules control the dynamics of electron transfer (ET). Here we tackle this problem using the charge-transfer-to-solvent (CTTS) transition of sodide (Na^-) [1].   Absorption of a visible photon by Na^- produces a localized excited state bound only by the polarization of the solvent, from which solvent motions promote electron detachment. Since the CTTS band of Na^- is similar in a variety of ethers and amines [2], we can use ultrafast spectroscopy to determine how the local solvent structure controls the dynamics of CTTS detachment. We find that there is a sub-ps delayed detachment of the electron from the CTTS excited state (Na^-*) followed by back ET (geminate recombination) on a time scale of a few ps.   For ether solvents, the back ET times correlate with solvent polarity, with more polar ethers having shorter back ET times. We also find that this trend does not hold in non-ether solvents, and there appears to be no correlation of the forward ET (detachment) time with solvent polarity. This points to the importance of local solvent structure in determining the CTTS detachment dynamics.
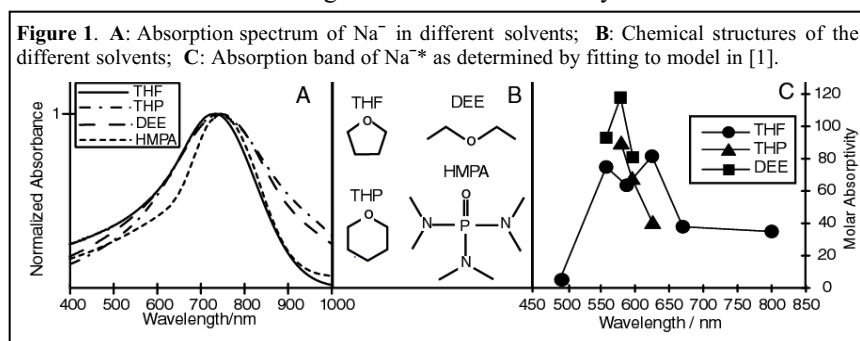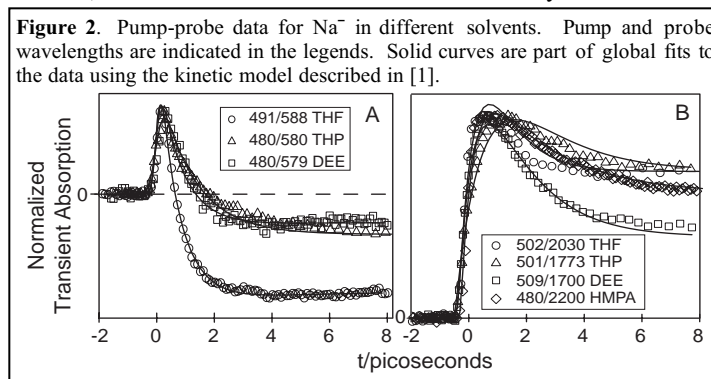

Figure 1. **A**: Absorption spectrum of Na^- in different solvents; **B**: Chemical structures of the different solvents; **C**: Absorption band of Na^-* as determined by fitting to model in [1].

Figure 1A shows the absorption spectrum of the Na^- CTTS transition in tetrahydrofuran (THF), tetrahydropyran (THP), diethyl ether (DEE), and hexamethylphosphoramide (HMPA); Figure 1B shows the chemical structures of each of these solvents. The spectrum of Na^- is similar not only in the three ethers but also the more polar HMPA. The ~2 μm absorption of the solvated electron in HMPA is also similar to that in ethers. This is a result of the diffuse nature of the positive dipole of HMPA and the difficulty for large HMPA molecules to form cavities around negative particles with radii smaller than 4-5 Å [3], leading

to a similar cavity size as for electrons in ethers. These factors also explain why the spectrum of Na$^-$ in HMPA is so similar to that in the ethers.

Figure 1C shows the visible transient absorption spectrum of the sodide CTTS excited state, Na$^-$*, as determined by fitting pump-probe data to a detailed kinetic model presented previously [1]. This species has its absorption maximum near 590 nm, the location of the sodium D line. The similarity of the spectrum in all solvents investigated supports our assignment of this absorption to a Na atom core that does not interact strongly with the surrounding solvent.[1]

Figure 2 shows pump-probe data for Na$^-$ excited at ~500 nm and probed at both ~580 nm and at ~2 μm. The solid curves are fits to the data using our kinetic model [1]. Probing at 580 nm monitors both Na$^-$* and the ground state bleach of Na$^-$, while probing at 2 μm monitors solvated electrons. In the three ether solvents, the 580-nm transient absorption is instrument-limited, and then decays as the electron detaches from Na$^-$* and the solvent rushes in to destroy Na$^-$* and create a solvated Na atom. Although the ejection mechanism is qualitatively similar, it is clear that the time for the forward ET, as measured by the decay of the Na$^-$* absorption, is quite different in the three ethers.

This conclusion is also supported by the matching rise times for the solvated electron's absorption at ~2 μm, which also reflect the e$^-$ detachment time. The back ET (geminate recombination) time scale is also different for each solvent. As shown in Table 1, the back ET times increase with decreasing solvent polarity for the ethers [4]. However, this trend does not include the highly polar solvent HMPA, in which the back ET time is considerably slower.

Figure 2. Pump-probe data for Na$^-$ in different solvents. Pump and probe wavelengths are indicated in the legends. Solid curves are part of global fits to the data using the kinetic model described in [1].

The trend in back ET times with solvent polarity, and the lack of such a trend for the forward ET times, suggests different mechanisms for the two ET processes. The initial photoexcitation of Na$^-$ produces a *p*-like state that must detach and localize into an *s*-like solvated electron. We believe that translational motions of the solvent molecules into the *p*-like angular node promote this detachment. In the fastest solvent, THF, inward translations of the nearly planar ring can be assisted by translation-rotation coupling, as seen previously in MD simulations [5]. In the next-fastest solvent, DEE, we believe that free rotation about the C-O bond decreases the ability (relative to THF) of the first-shell molecules of this solvent to undergo inward translation. Finally, for slow THP, it is likely that packing of the solvent into chair-like structures makes it difficult for the first-shell solvent molecules to translate into the angular node, resulting in

a slower response. This type of packing effect is also seen in the pronounced liquid structure for nearest neighbors in the related solvent, cyclohexane [6].

Table 1. ET times for Na⁻ in solvents with different dielectric properties; the dielectric values are taken from [4]. The ET times have an uncertainty of ±0.05 ps.

solvent	abbreviation	$\varepsilon/\varepsilon_0$	μ / D	ET Times (ps) forward	reverse
diethyl ether	DEE	4.42	1.15	0.82	1.53
tetrahydropyran	THP	5.68	1.63	1.26	1.38
tetrahydrofuran	THF	7.47	1.75	0.70	0.78
hexamethylphosphoramide	HMPA	29.00	5.55	0.41	2.51

In contrast to detachment, the fast back ET is due to the recombination of contact pairs [1] in which the sodium atom is in the electron's first solvation shell. The recombination progresses via a nonadiabatic transition, the rate of which depends on the overlap of the electron's wave function with its geminate Na atom partner. This is why the macroscopic dielectric properties of the solvent become important in stabilizing the contact pair: the less polar the solvent, the better solvated the neutral sodium atom and the less favorable the back ET.

The large differences in the CTTS dynamics in very polar HMPA likely are due to a different molecular solvent structure. The bulky nature of this solvent creates large cavities even before electron detachment [3]. Thus, the forward detachment can proceed rapidly since little solvent translational motion is needed, and the unusually high stability of the newly-formed solvated electron cavity could then result in the observed slow back ET time

Overall, the results show that it is not sufficient to consider only the dielectric properties of a solvent when considering ET dynamics. The local molecular structure of a solvent can have direct effects on the motions that control the dynamics of ET. For the Na⁻ CTTS reaction in weakly polar ether solvents, the forward ET time is dictated primarily by the local solvent structure, whereas the back ET depends mostly on solvent polarity. For the bulky polar solvent HMPA, the slow back ET reaction likely is due to the tendency for the solvent to form unusually stable cavities for the solvated electron.

References

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