Femtosecond Studies of the Charge-Transfer-to-Solvent Transition of the Sodium Anion in THF

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Abstract. Following excitation of the CTTS band of the sodium anion in THF, recombination of the solvated electrons with the parent sodium atom takes place on two time scales: ~2 ps, and ~200 ps. The fraction of electrons that recombine in ~2 ps depends on the initial excitation energy; the data suggest that a stable atom:electron contact pair is formed following CTTS. All the results show that Na⁻ provides a unique model system for studying charge transfer: only electronic degrees of freedom are involved, so that the spectroscopy is well-defined for all the species in the reaction.

1. Introduction

The detailed dynamics underlying charge transfer reactions is of great interest in chemical physics. The simplest example of such reactions is that of the charge-transfer-to-solvent (CTTS) transitions of atomic anions; excitation of the CTTS band produces a neutral atom and a solvated electron. While most of the attention has focused on aqueous halides, the halides are challenging to study because the time scales for charge transfer are exceedingly fast (≤ 200 fs) and because the relevant spectroscopic transitions are deep in the UV [1].

Recently, we have explored the CTTS dynamics following excitation of Na⁻ in THF [2]. Our choice was predicated by spectroscopic convenience: both the Na⁻ CTTS ground and excited states, and the absorptions of both the solvated electron and the Na atom, are easily and independently accessible in the visible or IR [2].

In this paper, we explore the dynamics of recombination between the ejected electron and the neutral Na atom following CTTS excitation. We find that this back electron transfer takes place on two very different time scales, suggesting that the CTTS electron is bound in a contact pair with the neutral atom product.

2. Experimental Methods

The pump-probe experiments utilize a regeneratively amplified Ti:Sapphire laser that produces 1 mJ, ~100 fs pulses near 800 nm at a 1 kHz repetition rate. These pulses pump a dual-pass OPA to produce light at ~2 μm for probing solvated electrons in THF. The visible pump light is produced by sum-frequency mixing the residual 800 nm fundamental with either the OPA signal or idler. Details on the set-up of the pump-probe spectrometer are described elsewhere [2].

Samples of Na⁻ were prepared following a modification [2] of the procedure of Dye [3]. The basic idea is to shift the equilibrium $2\,Na_{(s)} \leftrightarrow Na^+ + Na^-$ to the right by complexing the sodium cation with the addition of a crown ether.

3. Results and Discussion

Figure 1 summarizes the spectroscopy of the Na^- CTTS system. The heavy solid curve is the UV-visible absorption of Na^- in THF: excitation of this band produces a Na atom and a solvated electron. Note that the acronym CTTS is somewhat of a misnomer: the CTTS excited state is *localized,* bound not only by the nuclear attraction of the electron to the Na core but also by the polarization of the solvent [4]. It is solvent motion subsequent to the excitation that causes the electron to detach; the Franck-Condon excitation does not directly produce a solvated electron.
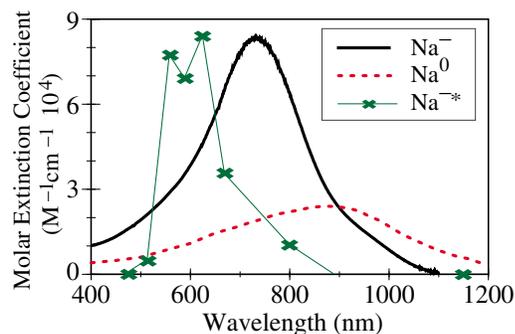
Fig. 1: Absorption of species involved in the Na^- CTTS reaction.

The dashed curve in Fig. 1 shows the spectrum of the solvated Na atom in THF [5]. This species could be described as a Na^+/solvated electron contact pair [5]; however, a species with this absorption spectrum is detected immediately following CTTS electron detachment [2]. As will be shown below, a significant fraction of geminate recombination occurs within 2 ps of the CTTS excitation. Since it is unlikely that a 3-body recombination event can take place on this time scale, we believe that the species whose absorption is represented by the dashed curve in Fig. 1 is better described as a solvated neutral Na atom.

Finally, the symbols in Figure 1 show the absorption spectrum of the CTTS excited state prior to electron detachment, as determined by fitting a variety of pump-probe transients to a kinetic model [2]. The strong absorption near 590 nm is reminiscent of the gas phase absorption spectrum of neutral sodium. The error bars on the data (not shown) are larger than the apparent structure near 550 nm.

Figure 2 shows the results of femtosecond pump-probe experiments which monitor the ~2 μm absorption of the THF-solvated electron following excitation at a variety of visible wavelengths. The left panel shows the dynamics in the first 8 ps following excitation, with the data normalized to the same maximum change in absorbance. The right panel shows the data on a much longer time scale; here, the data have been normalized to the same change in absorbance at 8 ps delay.

The ~700 fs rise of the absorption in Fig. 2(a) corresponds to the time needed for solvent motions to cause the electron to detach from the CTTS excited state [2]. The rapid decay on the ~2 ps time scale is independent of probe wavelength, verifying that it results from geminate recombination, or back electron transfer.

The amount of back electron transfer changes drastically with excitation wavelength but the time scale does not. This suggests multiple pathways for charge transfer. Following CTTS excitation, electrons are ejected to a nearby

solvent cavity. Since the electronic wavefunction is highly delocalized in non-polar solvents like THF, there is some probability of overlap with the Na atom parent, leading to the possibility of recombination via direct non-adiabatic
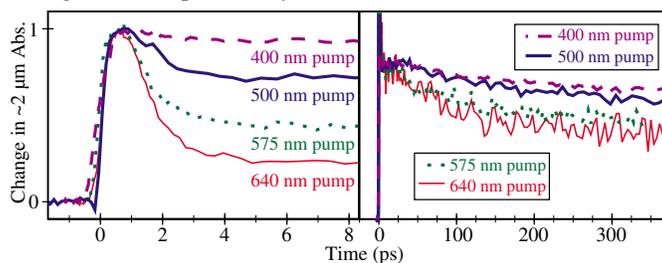
Fig. 2: 2 µm pump-probe transients for Na⁻ at different pump wavelengths

transition. At blue excitation wavelengths, the electron is ejected further into the solvent, reducing the overlap. The right panel of Fig. 2 makes it clear that those electrons which do not recombine in ~2 ps do not recombine for at least hundreds of ps. This long time recombination cannot be diffusive. Fits to standard diffusive recombination models give a thermalization distance ≥ 45 Å; a visible photon cannot eject electrons this far (especially given that some fraction of them are close enough to recombine directly within 2 ps). Thus, an electron ejected by CTTS forms a contact pair with the parent atom. If the electronic wavefunction overlaps the parent, recombination occurs quickly. If the electron localizes just a small distance further away (solvent-separated pair), there is no overlap and recombination cannot take place until a significant solvent fluctuation occurs. Diffusion does not appear to play any important role in the recombination process.

4. Conclusions

Overall, if the solvated electron's wavefunction has overlap with the neutral partner, then recombination can take place via a direct non-adiabatic transition on a time scale ≤ 2 ps. If there is no such overlap, on the other hand, recombination is inhibited (taking ≥ 200 ps) because there is a large free energy barrier to break up the local solvent structure around the contact pair: in other words, the back electron transfer can be thought of as occurring in the Marcus inverted regime.

References

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