# Control of an electron transfer reaction using a sequence of femtosecond pulses

Ignacio B. Martini; Erik R. Barthel; Benjamin J. Schwartz

Department of Chemistry, University of California, Los Angeles; Los Angeles, CA, 90095
tel: 310-206-4113, fax: 310-206-4038; Schwartz@chem.ucla.edu

**Abstract:** A sequence of femtosecond laser pulses is used to control the electron transfer dynamics of sodide in solution. The electron recombination can be either enhanced or suppressed depending on the electron re-excitation delay time.

We report the optical control of electrons during a Charge-Transfer-to-Solvent (CTTS) reaction. The picosecond and sub-picosecond CTTS dynamics of sodide ($Na^-$) in tetrahydrofuran (THF) has been extensively studied.[1-4] The basic picture of this photoinduced electron transfer reaction is summarized in Figure 1.[1] Upon photoexcitation, the excess electron is promoted to a "*p*-like" state, and subsequent molecular solvent motions induce the delayed detachment and localization of the electron near the $Na^0$ partner. At low excitation energies the electron is ejected to the same solvent cavity that contains the sodium atom, into an *immediate* contact-pair. These species share significant wave function overlap that leads to direct nonadiabatic recombination in ~1 ps. In contrast, higher excitation energies produce *solvent-separated* contact pairs that reside one or more solvent shells away from the sodium atom. Negligible wave function overlap prevents rapid recombination, which happens on the hundreds-of-picoseconds timescale. The relative number of electrons ejected into immediate and solvent-separated pairs can be smoothly adjusted by tuning the excitation energy across the visible CTTS absorption band.[1] Finally, *free* electrons are also created by high-energy excitation and possibly by dissociation of solvent-separated contact pairs. The free electrons have lifetimes longer than nanoseconds.

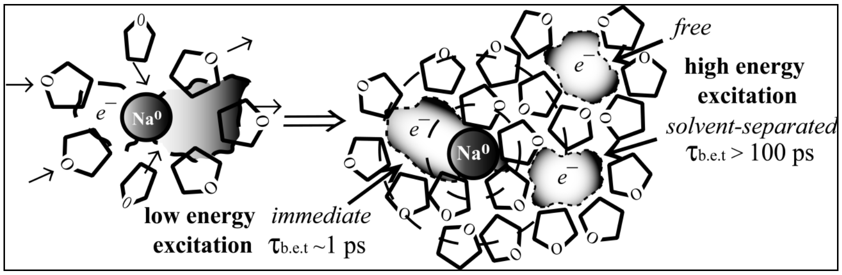

Fig. 1. Schematic representation of the different kinds of sodium-solvated electron contact pairs created in the sodide CTTS reaction.

By taking advantage of the vastly different recombination rates of the two types of contact pair electrons and the great separation of the absorption spectra of the electron and the sodide parent (Figure 2A), we designed a three-pulse experiment to modify the population dynamics of the recombining electrons.[2,3] A 780-nm pulse is used to excite $Na^-$ and create a distribution of solvated electrons with most in immediate contact pairs. A second pulse at 2000 nm then excites predominantly electrons in immediate contact pairs if it arrives at the sample within the first 3 ps of the initial pump. At times later than 3 ps, all the immediate pairs have recombined, so the re-excitation pulse acts exclusively on electrons in solvent-separated contact pairs and free electrons. A third pulse is used to probe the resulting dynamics by monitoring the $Na^-$ bleach recovery at 480 nm or the electron absorption at 1250 nm. This type of electron re-pump experiment is similar to that recently performed by Barbara and co-workers.[5,6]

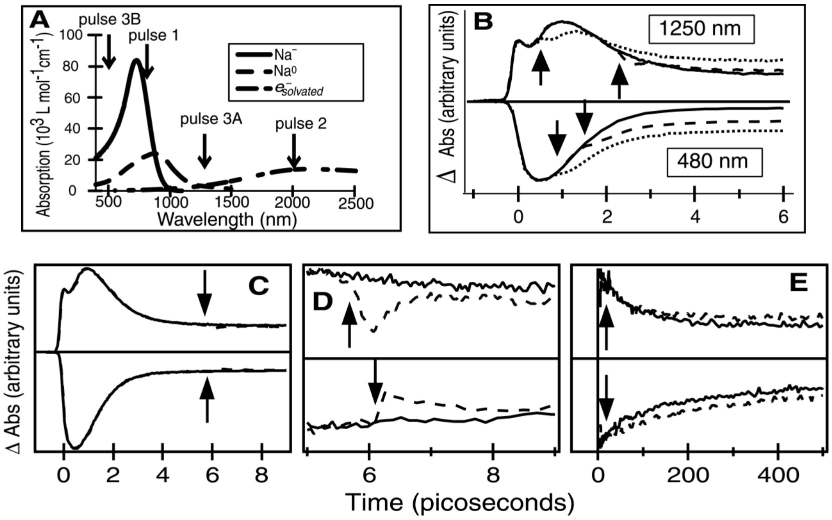

Fig. 2. **A** Absorption spectrum of all the species involved in the CTTS reaction of sodide in THF. **B-E** The solid lines represent the regular pump-probe data of the CTTS reaction of sodide in THF after 780 nm excitation. The positive signals correspond to the transient absorption of the electron probing at 1250 nm, while the negative transient bleach is probed at 480 nm. The dashed lines correspond to the three-pulse experiments, with the 2000 nm light interacting with the sample at different delay times indicated by the arrows. **B** is the three-pulse experiment performed on the immediate contact pairs, **C** is the three-pulse experiment performed on the solvent-separated contact pairs, **D** is a magnification of **C**, **E** is the long time dynamics of **C**.

The solid curves in Figures 2B-E show the results of regular two-pulse pump-probe experiments over different time scales. The upper panels reflect the 1250-nm $e^-$ absorption dynamics, while the lower panels show the 480-nm $Na^-$ bleaching dynamics. The CTTS photodetachment is represented by the slow rise (~700 fs) of the electron absorption signal (positive signals, the pulse-width limited component is explained elsewhere [3]). The negative bleach signal, on the other hand, appears instantaneously, and both traces decay at short times (<3 ps) due to the nonadiabatic geminate recombination of the electrons in immediate contact pairs (Figs 2B&C). The hundreds-of-ps decay presented in Fig 2E corresponds to the recombination of electrons in solvent-separated contact pairs.

The dashed and dotted curves in Fig. 2B-E present the effect of the 2000-nm electron re-excitation pulse on the recombination reaction. Re-excitation of immediate contact pairs (Fig 2B) is achieved by applying the second pulse within the first 3 ps after the initial 780 nm pulse, while solvent-separated contact pairs are excited at delay times longer than 4 ps (Figs. 2C,D&E).

A larger signal offset is observed for the three-pulse experiment performed on immediate contact pairs, as well as at long times for the solvent-separated contact pairs (Figs 2B&E). This indicates that the effect of the second pulse is to produce more electrons and less $Na^-$ at long times than would have been created with just the initial pump pulse. This result is explained as a partial suppression of the geminate recombination of both kinds of contact pairs. On the other hand, the instantaneous effect of the 2000-nm light on solvent-separated contact pairs is a decrease in the size of the signal offset (Figs 2C&D), which is assigned to enhanced recombination. Thus, the immediate effect of the second pulse is to decrease the number of electrons relative to that produced by the initial pump.

The microscopic dynamics of the three-pulse experiment can be explained with the help of Figure 1. Upon excitation, the solvated electron is promoted to a quasi-continuum state, characterized by a large delocalization of the electronic wave function.[2,3] The excited immediate contact pair electron will now access regions of the solvent further away than its original solvent cavity. The electron can now re-localize, effectively transforming into a solvent-separated contact pair or a free electron, thus shutting off the rapid immediate nonadiabatic geminate recombination. Likewise, the original solvent-separated contact pairs can convert into either free electrons, shutting off the long time recombination, or into immediate contact pairs, with the latter resulting in enhancement of the geminate recombination. A detailed analysis of the number of solvent-separated electrons that recombine upon excitation suggests that recombination must occur both from the excited and ground states of the solvated electron.[3]

To the best of our knowledge, this is the first time a charge transfer reaction reaction has been photo-controlled during the process of electron transfer.

## References

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