

Ultrafast Excited-State Electron Transfer at an Organic Liquid/Aqueous Interface

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Electron transfer (ET) at an interface is a critical process in many chemical and biological systems. A recent body of work has explored the ultrafast aspects concerning the dynamics of intermolecular ET in bulk liquids.^{1–5} Recently, developments in spectroscopy,^{6,7} scanning electrochemical microscopy (SECM),^{8,9} and other techniques^{10–12} are allowing investigation of intermolecular ET in the asymmetric environment of liquid/liquid interfaces, requiring however, that the two liquids have supporting electrolytes.^{13–19} Despite the fact that these electrochemical methods provide valuable insight, features such as diffusion^{9,17,20} and the requirement of ion transport^{9,21} across the liquid/liquid interface to maintain electroneutrality in each liquid can obscure the microscopic characteristics of the process. For the first time, in the work reported here, the ultrafast dynamics of ET at a liquid/liquid interface was observed in real time using femtosecond lasers. On the basis of an earlier approach²² we choose the donor molecule to serve as one of the solvents composing the interface which allows us to minimize distance between donor and acceptor, thus eliminating translational diffusion as a key step in the ET kinetics. Coupling this with the interface selectivity of second harmonic generation (SHG) makes it possible to observe interfacial equilibrium and dynamic processes concerning ET without interference from the bulk media forming the interface.²³

In this communication the time-resolved ultrafast excited state ET at the dimethylaniline (DMA)/aqueous interface is presented. Photoexcited coumarin 314 (C314) and DMA respectively serve as acceptor and donor molecules. The coumarin dye was selected because of its strong SHG signal at $2\times$ the fundamental probe frequency and because of our extensive knowledge of its equilibrium and dynamic processes at aqueous interfaces.²⁴

Following the photoexcitation of C314 (eq 1) with a 120 fs laser pulse at 424 nm, the time-dependent changes of the C314 ground- and excited-state populations were probed with a 140 fs pulse at 832 nm. By selecting 832 nm the SHG generated is resonant with C314, and consequently the detected SHG is dominated by ground- and excited-state C314, i.e., the contributions of interfacial DMA and water to the SHG signal are small and, furthermore, are essentially constant in time because of their very high interfacial populations. In its excited state the electron affinity of C314 is sufficient to effect an ET from a ground-state DMA molecule (eq 2), thereby producing the radical anion C314^{•-} and the radical cation DMA^{•+}. After this ET step, the back electron transfer (BET) from C314^{•-} to DMA^{•+} yields the neutral ground-state C314 and DMA molecules (eq 3).

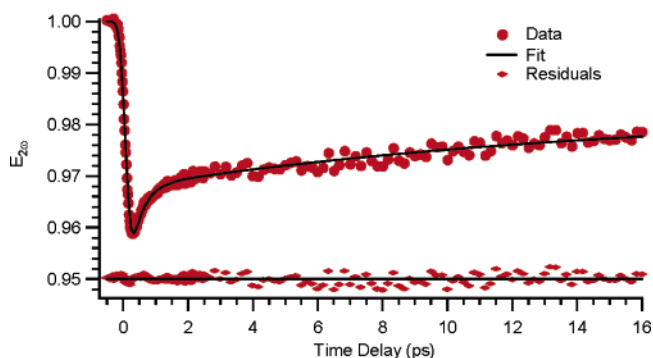
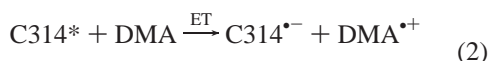


Figure 1. Dynamics of excited-state C314.

In our experiments C314 is adsorbed to the DMA/water interface where its interface population was determined to be $\sim 10^{13}$ C314/cm², from interfacial tension measurements.²⁵ Dynamics were monitored by time-resolved pump–SHG probe measurements using a Ti-sapphire regeneratively amplified laser (Clark MXR) in reflection geometry. The SHG signal was detected using a PMT which is then boxcar integrated (Stanford Research Systems) and then recorded by computer (National Instruments A/D card).

Dynamics of the excited-state C314 is characterized by a biexponential fit which is convoluted to include the instrument response time (Figure 1). The observed ultrafast decrease in the second harmonic field, $E_2\omega$, at the time of photoexcitation, $t = 0$, is due to the bleaching of ground-state C314 molecules. In addition, the amplitude of $E_2\omega$ is reduced because the phase of the initially resonant excited-state, C314*, is opposite to that of ground state, C314, which results in a cancellation and therefore a further reduction in the SHG signal.

The extracted times are $\tau_1 = 362 \pm 60$ fs with an amplitude of 0.53 and $\tau_2 = 14 \pm 2$ ps with an amplitude of 0.47. The 362 fs component is attributed to the excited-state C314* solvation dynamics at the DMA/aqueous interface; this solvation occurs in a time scale similar to that of C314* solvation at an air/aqueous interface,²⁴ average of 850 ± 70 fs, and similar to that of C314* solvation at a neutral surfactant (stearic acid) monolayer/aqueous interface, 400 ± 60 fs. It should be noted that the SHG signal increases as solvation of C314* occurs because the solvation of C314* results in a Stokes shift. Because the energy difference between the solvated C314* with its ground state is no longer equal to the probe wavelength, it follows that the contribution of the C314* to the SHG signal is reduced. Since the C314* contribution to the SH signal is reduced, the cancellation is diminished, and as a result the signal increases as seen in Figure 1. The longer-time component of 14 ps (Figure 1) is assigned to ET from DMA to excited-state C314*.

To confirm that the 14 ps component is due to ET dynamics and not the dynamics of other processes we probed the time

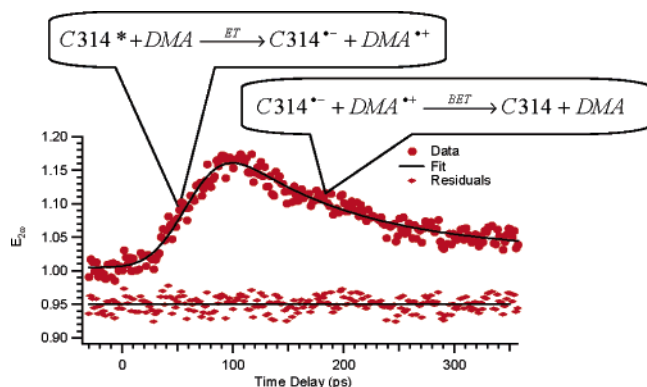


Figure 2. Dynamics of formation and decay of DMA^{•+}.

evolution of the radical cation DMA^{•+}. As given in eq 2 the transfer of an electron from DMA to C314* generates the DMA^{•+} radical cation. The formation of DMA^{•+} thus tracks the ET process. To selectively follow the DMA^{•+} dynamics we use a probe wavelength of 904 nm that generates an SHG signal that is resonant with the ground- to lowest excited-state transition²⁶ of DMA^{•+} giving a large resonant enhancement of the SHG signal. In this way the SHG signal is dominated by DMA^{•+} with C314*, C314, DMA, and water contributing to a weak background signal. A confirmation of the DMA^{•+} dominance in the SHG signal is the absence in Figure 2 of the initial bleach due to C314 seen in Figure 1. Figure 2 shows the time evolution of the DMA^{•+} radical cation.

The formation time, 16 ± 3 ps, of the DMA^{•+} is conclusive evidence of the ET dynamics, in agreement with the 14 ± 2 ps obtained from the coumarin dynamics. The BET time constant is 163 ± 4 ps, from which we infer that the radical ions do not diffuse more than ~ 10 Å from each other, i.e. they remain in the interfacial region of ~ 10 Å.

Although there have been no studies of ET from photoexcited C314 to DMA in the bulk liquid DMA, there have been a number of studies of other coumarins in bulk DMA,^{1–3} most of which show a biexponential decay of the photoexcited coumarin. The two decay times in the bulk DMA studies with C153, which has a reduction potential very close to that of C314 (10 mV difference), are 3 and 25 ps. Our results are not very different from those of the bulk DMA studies. Considerable work on ET at the liquid/liquid interface has been performed using electrochemical and photocurrent methods. Comparison with these results is difficult since the measurements yield heterogeneous rate constants in units of cm/s. Converting to units of 1/s requires knowledge of an effective length^{16,17} over the interfacial region where the process occurs which is ambiguous. In addition, the electrochemical experiments require that both liquids have supporting electrolytes. To enable detection of the product species (that are generated by the ET) they must

diffuse to the working electrode. However, for the radical ion to leave the interface, a supporting electrolyte ion must cross the interface as well to maintain electroneutrality in each liquid. This can result in a rate constant which is different from the microscopic rate constant for ET. Studies are underway to further elucidate microscopic details of ET at the liquid/liquid interface.

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Supporting Information Available: Experimental details, sample preparation and relative energy levels. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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