On the insensitivity of the non-adiabatic relaxation of solvated electrons to the details of their local solvent environment

Ignacio B. Martini, Benjamin J. Schwartz *

Department of Chemistry and Biochemistry, University of California at Los Angeles, 2077A Young Hall, Los Angeles, CA 90095-1569, USA

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Abstract

Utilizing the charge-transfer-to-solvent transition of Na^-, we measure the excited-state lifetime of the solvated electron (e_s^-) in tetrahydrofuran (THF) in each of three different well-defined local solvent environments: an isolated THF cavity, a THF cavity with a sodium atom located one solvent shell away, and a THF cavity with a sodium atom in the first solvent shell. We find that the excited-state lifetimes of the e_s^- in each environment are the same, suggesting that the solvent-induced non-adiabatic coupling that determines the radiationless transition rate is insensitive to the details of the specific atoms or molecules in the first solvent shell. © 2002 Elsevier Science B.V. All rights reserved.

The dynamics of chemical reactions in solution are strongly affected by solvent molecules whose motions are coupled to the electronic states of the reactant. One of the most important effects is non-adiabatic coupling, in which the adiabatic potential surfaces of the reacting species are mixed together due to rapid nuclear motions of the solvent, a manifestation of breakdown of the Born–Oppenheimer approximation [1]. Thus, non-adiabatic coupling allows for solvent-induced transitions between reactant energy levels. These transitions can provide access for a reacting system to enter new regions of phase space, permitting the creation of new products or significantly altering reaction rates. Non-adiabatic coupling is particularly important in electron transfer reactions, in which the reaction coordinate can consist mostly or entirely of the nuclear motions of the solvent [2].

One of the prototypical systems for studying solvent-induced non-adiabatic coupling has been the solvated electron (e_s^-). Solvated electrons are confined within a solvent cavity; the eigenstates of such excess electrons are similar to those of a particle in a finite spherical box. Solvent molecule motions are strongly coupled to the energy levels of this solute: even subtle changes in the size and shape of the solvent cavity lead to large modulation of the electronic energy levels [3]. The importance of this coupling is reflected in the short excited-state lifetime of the e_s^-: the solvent-induced

* Corresponding author. Fax: +1-310-206-4038.
  E-mail address: schwartz@chem.ucla.edu (B.J. Schwartz).

mixing of the ground and excited states is so strong that photo-excited solvated electrons return to their ground state in under a picosecond [4–7], despite expected radiative lifetimes in the nanosecond regime [8]. The excited-state lifetime of solvated electrons has been investigated theoretically by several groups [9–13], including calculations by Prezhdo and Rossky [14–16] that directly addressed the specific solvent motions that non-adiabatically couple the ground and excited electronic states. The theoretical lifetime predictions are in good general agreement with experiments performed on solvated electrons in water and alcohols by several groups [17–19], including a series of detailed studies by Barbara and co-workers [4–7].

While it is clear that changing solvents affects the excited-state lifetime of the e_s^-, there has been no experimental work addressing how the details of the local solvent structure alters the non-adiabatic coupling that controls the electron's lifetime. This is because it is extremely difficult to prepare solvated electrons in different well-defined local solvent environments. In this Letter, we show how we have overcome this difficulty, allowing us to measure the relaxation dynamics of the solvated electron in tetrahydrofuran (THF) in three different well-defined local solvent environments. We find that whether the e_s^- is in an isolated THF cavity, a THF cavity with a sodium atom located one solvent shell away, or a THF cavity with a sodium atom in the first solvent shell, the excited-state lifetime is the same. This suggests that it is not just the motions of the nearest molecules that control the electron's lifetime, but that the solvent motions that control non-adiabatic coupling are spread throughout the solvent, a result with important implications for condensed-phase chemical reaction dynamics.

The usual method for creating solvated electrons is by multiphoton ionization of the solvent (or of an easily ionizable solute, such as I^- or $[Fe(CN)_6]^{4-}$). The initial ionization produces conduction band electrons with a great deal of kinetic energy. These hot, delocalized conduction band electrons can travel through the solvent before they ultimately localize into cavities, leading to a continuous distribution of distances between the localized electrons and the parent species from which they were generated [20]. Because of this, e_s^- excited-state dynamics are typically studied in experiments that use three ultrafast laser pulses. The first pulse is used to synthesize the electrons via multiphoton ionization. The second and third pulses, which are used to perform pump–probe spectroscopy on the freshly created solvated electrons, are not applied until after the localization is completed. In this way, the experiments are able to measure the excited-state lifetimes starting from fully relaxed solvated electrons [4–8,17–19].

For the experiments discussed here, we generated solvated electrons via a different route, making use of the charge-transfer-to-solvent (CTTS) [21] transition of the sodium anion (Na^-) in THF (Fig. 1a, solid curve) [22,23]. We have extensively studied this reaction and elucidated the molecular details of the CTTS electron detachment process [24–26], which are illustrated schematically in Fig. 1b. We found that upon photoexcitation, the solvent reorganizes around the newly created CTTS excited state, causing the electron to detach and localize in a nearby solvent cavity. Excitation into the low energy side of the CTTS band (near 800 nm) predominantly creates electrons that reside in the same solvent cavity as their sodium atom (Na^0) partners; we refer to these species as 'immediate' contact pairs (Fig. 1b, left). The wavefunction of an immediate-pair e_s^- has significant overlap with the Na^0 in the first shell, leading to rapid back electron transfer (geminate recombination) to reform Na^- within a couple of picoseconds. Excitation on the high-energy side of the CTTS band (near 400 nm), on the other hand, produces solvated electrons that are located one solvent shell away from their sodium atom partners (Fig. 1b, right). The wavefunctions of these 'solvent-separated' contact pair electrons do not overlap with their geminate partners and recombine on the hundreds-of-picoseconds time scale. High excitation energies also produce a few 'free' solvated electrons that are ejected to locations in the solvent further away than the second solvent shell (Fig. 1b, right). These electrons do not recombine with their Na^0 partners on sub-ns time scales. The initial distribution of electrons localized at the three different distances from their Na^0 partners changes
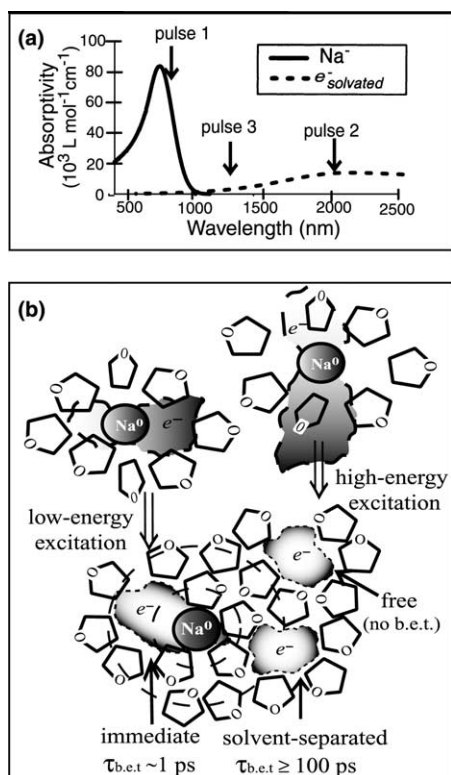
Fig. 1. (a) Absorption spectra of the Na^- CTTS band (solid curve, [22,23]) and the e_s^- (dashed curve [29,30]) in THF. The arrows show the spectral positions of the ultrafast laser pulses used in the experiments. (b) Schematic representation of the CTTS reaction of Na^- in THF [26]. Low-energy CTTS excitation produces a p-like excited state contained inside the original solvent cavity which then detaches into an immediate contact-pair (left). Higher-energy excitation generates a spatially extended p-like state that extends beyond the original solvent cavity (upper right). Depending on the degree of delocalization, the electron can then detach either into a solvent-separated contact pair, or a free solvated electron (lower right).

smoothly as the excitation wavelength is tuned through the CTTS absorption band, providing a convenient method for producing electrons in different local solvent environments [24–26].

In addition to distinguishing the local environments of the CTTS-detached electrons via their recombination dynamics, we also have verified the existence of immediate and solvent-separated contact pair electrons using a sequence of ultrafast pulses that controlled the back electron transfer reaction [27,28]. In these experiments, electron

detachment was initiated with a 780-nm pulse that created a majority of immediate contact pairs plus a smaller number of solvent-separated contact pairs. A second pulse, tuned to the electron's absorption maximum near 2000 nm (Fig. 1a, dashed curve) [29,30], was then applied at different delay times to act selectively on electrons in different local environments. We found that application of the 2000-nm pulse at early times transformed a significant fraction of immediate contact pair electrons into solvent-separated contact pairs, reducing the amount of short-time geminate recombination. This suggests that one of the effects of 2000-nm excitation is to *relocalize* a e_s^- into a cavity one solvent shell away. The 2000-nm pulse also was applied to electrons in solvent-separated contact pairs by delaying its arrival until times after the immediate contact pairs had recombined. We found that geminate recombination of the solvent-separated electrons was enhanced at early times and hindered at longer times, consistent with the idea that the 2000-nm excitation pulse leads to electron relocalization. The fact that 2000-nm excitation has a different effect on the recombination dynamics when applied at different times verifies that the CTTS-produced solvated electrons are indeed in different local solvent environments [27,28]. Here, we will take advantage of the ability to selectively excite solvated electrons in different environments to explore the effects of the local solvent structure on the non-adiabatic coupling that determines the electron's excited-state lifetime.

The sodium anions whose CTTS photodetachment allows us to create solvated electrons in different local environments were synthesized in THF based on literature procedures [31]; full details of the sample preparation have been presented previously [24,32]. For the data presented below, highly concentrated samples (OD ~ 4 in 1 mm at the 720-nm CTTS absorption maximum) were used to improve the signal-to-noise ratio. We did verify, however, that no changes in dynamics were observed for samples with a wide range of concentrations.

The experiments were performed with a regeneratively amplified Ti:Sapphire laser system that produces 1 mJ pulses of ~ 120 fs duration,

centered at 780 nm at a 1 kHz repetition rate. Full details of the experimental setup are given elsewhere [28,33]. Briefly, a small portion of the 780-nm fundamental light was used to initiate the CTTS electron detachment (pulse 1 in Fig. 1a) while the remainder of the fundamental light was used to pump an optical parametric amplifier (OPA). For some experiments, the first pulse was doubled to 390 nm in order to enhance the yield of solvent-separated and free electrons. The second pulse, the idler beam from the OPA at ~ 2 μm (pulse 2 in Fig. 1a), served to re-excite the electron near its absorption maximum at selected delay times after the pump. The signal beam from the OPA, at ~ 1250 nm, was then used to probe the e_s^- on the blue side of its absorption band (pulse 3 in Fig. 1a). We tried experiments using all polarization combinations for the 780-nm pump and 2000-nm re-excitation pulses, but found no effect of relative polarization on any of the measured dynamics. We note, however, that at higher time resolution, Ruhman and co-workers [34] observed changes in Na^- CTTS dynamics with different excitation polarizations that we were unable to see. Thus, it is possible that polarization could have an effect in the three-pulse experiments described here at times faster than our ~ 200 fs instrument response.

The goal of the experiments presented here is to measure the excited-state lifetime of the immediate contact pair electrons, solvent-separated contact pair electrons, and free solvated electrons created by CTTS photodetachment from Na^-. Each of these electrons is in a well-defined local environment (characterized by the presence or absence of a sodium atom in the first or second solvent shell), and each can be excited selectively by application of the ~ 2000-nm pulse at the appropriate time after CTTS excitation. The excited-state lifetime can then be measured by probing the recovery of the electron's absorption at 1250 nm. The 2000-nm excitation pulse, however, not only excites the solvated electrons but also alters their recombination dynamics. Thus, in order to extract cleanly the excited-state lifetime of the electron from our 1250-nm probe experiments, we need to understand how the recombination dynamics are altered by the 2000-nm excitation.

The solid circles in Fig. 2a show the results of a two-pulse pump–probe experiment in which the Na^- CTTS band was excited at 780 nm and the resulting dynamics were probed at 1250 nm. This signal presents an instrument-limited rise and fast decay that we assign to a CTTS excited-state absorption whose frequency and oscillator strength are altered by solvation dynamics [32]. The solvent motions that respond to CTTS excitation also create a cavity into which the electron can detach and localize in ~ 700 fs [26], as reflected by the subsequent rise of the 1250-nm signal. For 780-nm excitation, a large fraction of the detached electrons reside in immediate contact pairs that recombine in a few ps, producing a corresponding decay of the 1250-nm signal. The signal offset that remains at times $\geqslant 4$ ps is due to the presence of a small fraction of electrons in solvent-separated
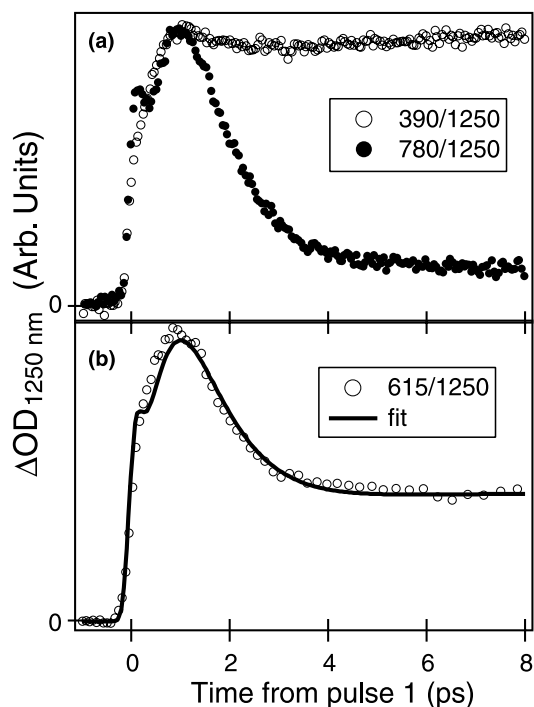

Fig. 2. (a) 1250-nm absorption dynamics following CTTS excitation of Na^- in THF at 780 nm (solid circles) and 390 nm (open circles). (b) 1250-nm absorption dynamics following Na^- CTTS detachment at 615 nm, (open circles) and a fit to the data using a $\sim 2:1$ linear combination of the traces in part a (solid curve).

contact pairs that do not recombine for hundreds of ps (cf. Fig. 1b). The open circles in Fig. 2a show the results of a similar experiment in which the Na^- CTTS band is excited at 390 nm. The data show the same features as for 780-nm excitation: an instrument-limited excited-state absorption followed by a ∼700-fs rise due to the appearance of detached solvated electrons, and then a decay over the next few ps resulting from the recombination of electrons in immediate contact pairs. The small amplitude of this decay and high offset at long times reflects the fact that 390-nm excitation produces mostly electrons in solvent-separated contact pairs and free electrons, with only a tiny fraction of the ejected electrons residing in immediate contact pairs.

The circles in Fig. 2b show the results of a similar experiment using 615-nm excitation. The data show all the same features as the traces in Fig. 2a but with a distribution of immediate and solvent-separated contact pair electrons that is roughly midway between that seen for 780 and 390-nm excitation. One of the nice features of the Na^- system is that for the $\leqslant 10$ ps time scales considered here, CTTS detachment effectively produces only two types of electrons: those that recombine within a few ps (immediate contact pairs), and those that do not (solvent-separated contact pairs and free electrons). This means that the recombination dynamics of electrons produced by an arbitrary CTTS excitation wavelength can be described as a linear combination of the individual dynamics of the electrons in immediate and solvent-separated contact pairs [25]. As an example, the solid curve in Fig. 2b is a fit of the 615-nm excitation data to a linear combination of the 780-nm (66%) and 390-nm (34%) excitation data presented in Fig. 2a. The fit is poor at early times, a result of the fact that the solvation dynamics that alter the 1250-nm CTTS excited-state absorption before the electron is ejected do not scale with excitation wavelength in a simple linear fashion. However, for times longer than ∼1 ps, after the electron ejection is complete, the fit describes the data perfectly. This is a manifestation of the fact that CTTS detachment produces electrons with only two different types of recombination kinetics [25,26]. Thus, we can use linear combinations of

the data in Fig. 2a to model the recombination dynamics of CTTS-detached electrons that have been re-excited at 2000 nm. With the ability to model the altered recombination dynamics, we can now proceed to measure how the excited-state lifetime of the e_s^- varies in each of the local solvent environments.

The solid curve in Fig. 3a shows the results of a 1250-nm probe experiment in which primarily immediate contact-pair electrons and some solvent-separated contact-pair electrons were created via 780-nm CTTS detachment from Na^- in THF; the offset at longer times is slightly higher than that shown in Fig. 2a because the excitation intensity was higher, leading to a small amount of 2-photon absorption that produced a higher fraction of solvent-separated contact pairs [25]. The dashed curve in Fig. 3a shows the results of the same
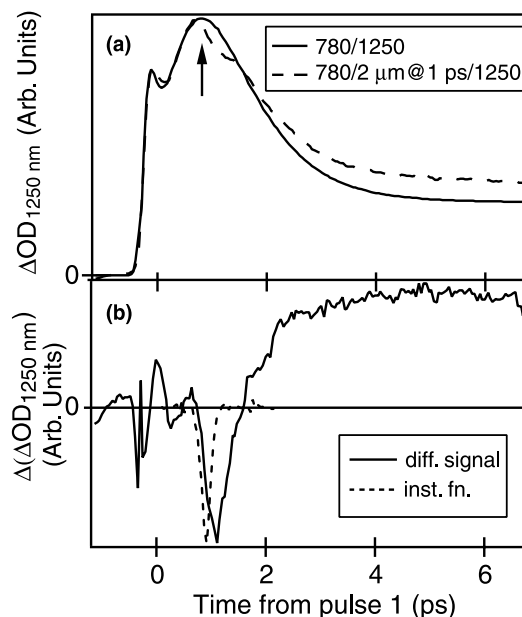

Fig. 3. (a) Comparison of two-pulse 780-nm pump/1250-nm probe (solid curve) and three-pulse 780-nm pump/2000-nm re-pump/1250-nm probe (dashed curve) experiments on Na^- in THF. The arrow marks the temporal arrival of the ∼2000 nm pulse in the three-pulse experiment, which acts primarily on electrons in immediate contact pairs. (b) Comparison of the difference signal (three-pulse minus two-pulse data in a, solid curve) and the cross-correlation between the 2000 and 1250-nm pulses (dotted curve).

experiment when a 2000-nm pulse is applied ∼1 ps after the initial 780-nm excitation (indicated by the arrow in the figure), a time at which the majority of the CTTS-detached electrons reside in immediate contact pairs. The difference between the two curves is a measure of the dynamics of just those electrons excited by the 2000-nm pulse; this difference signal is shown as the solid curve in Fig. 3b. The dotted curve in Fig. 3b shows the cross-correlation between the 2000 and 1250-nm pulses, revealing the instrument response and the time origin of the difference signal. The 2000-nm pulse places the electrons into an excited state, leading to an instrument-limited loss of the electron's ground state absorption at 1250 nm. The bleach of this absorption then recovers due to the electronic relaxation of the electron back to its ground state. In addition to reflecting the e_s^- excited-state lifetime, the difference signal in Fig. 3b also shows a positive component that results from the change in recombination dynamics induced by the 2000-nm pulse: the 2000-nm pulse leads to relocalization of some of the immediate-pair electrons into solvent-separated pairs and free electrons. In other words, there are more electrons present at long times than there would have been without the 2000-nm pulse, giving rise to the positive difference signal. Thus, the portion of the signal that represents the excited-state lifetime of the immediate-pair electrons is convoluted with the change in recombination dynamics.

We have already argued above that we can model the recombination dynamics upon 2000-nm excitation as a linear combination of the pump–probe scans shown in Fig. 2a. By fitting the long-time portion of the three-pulse signal in exactly the same manner as in Fig. 2b and then subtracting from the measured data, we should be left with a pump–probe signal that contains only the bleach recovery of the excited immediate-pair e_s^-. The results of this procedure are shown as the solid curve in Fig. 5. The subtraction is quite noisy at times before the arrival of the 2000-nm pulse (negative times in Fig. 5) for two reasons: first, the fit overestimates the number of solvent-separated contact pairs and free electrons before the 2000-nm pulse arrives, and second, the data at these early times include dynamics from the CTTS excited-state

absorption, as discussed above. By the time the 2000-nm pulse arrives, however, the CTTS excited-state decay is complete and the fit correctly represents the re-apportioned distribution of electrons in different environments, leading us to expect an accurate fit to the change in recombination dynamics. Thus, we believe that the corrected data at positive times shown in Fig. 5 provide an accurate window into the excited-state lifetime of immediate contact pair solvated electrons.

Given this measure of the excited-state lifetime of the immediate contact-pair electrons, the next logical question to ask is what are the excited-state lifetimes of free solvated electrons and solvated electrons in solvent-separated contact pairs? The solid curve in Fig. 4a shows the results of a 780-nm pump, 1250-nm probe experiment on Na$^-$ in THF, similar to that shown in Fig. 3a. The dashed curve in Fig. 4a shows the results of a related three-pulse experiment in which the 2000-nm pulse is applied to the electrons in solvent-separated contact pairs at a time delay of 5.8 ps, after all of the immediate pairs have recombined. The difference signal for this experiment is shown as the solid curve in Fig. 4b. As with the data in Fig. 3b, the difference signal shows an instrument-limited loss of optical density, the result of the bleach of the e_s^- ground state absorption upon application of the 2000-nm pulse. This bleach of the absorption then recovers within 1 ps as electrons relax from their excited state; however, the bleach does not recover completely. The negative offset indicates that one long-time effect of the 2000-nm pulse is to leave fewer electrons than there would have been without the 2000-nm pulse, the result of enhanced back electron transfer from the excited state [27,28].

The dotted line in Fig. 4b shows the difference signal for a similar set of experiments in which the initial excitation was at 390 nm and the 2000-nm light arrived ∼500 ps later. The 390-nm pump pulse produced a large initial population of free electrons, and after 500 ps, any immediate contact pair electrons and most of the solvent-separated contact pair electrons have recombined. Thus, the difference signal in this experiment reflects primarily the relaxation dynamics of free electrons, although there is a small component resulting from the few remaining solvent-separated electrons, as
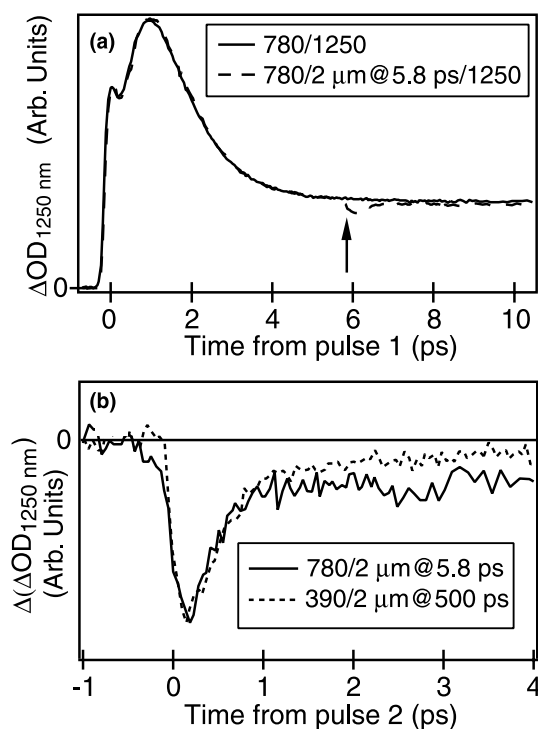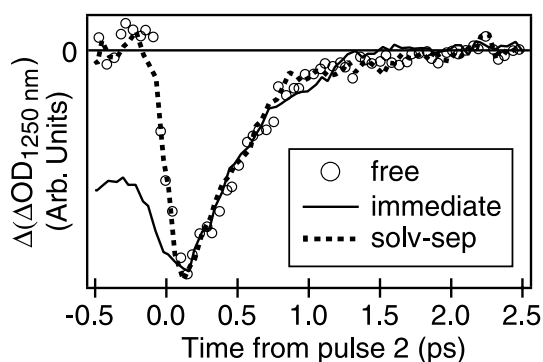
Fig. 5. Recombination-corrected (see text) difference signals for immediate contact-pair electrons (solid curve; cf. Fig. 3b), solvent-separated contact-pair electrons (dotted curve, cf. Fig. 4b), and free electrons (open circles; cf. Fig 4b). These traces represent the excited-state relaxation dynamics for the THF-solvated electron in each local environment.

Fig. 4. (a) Comparison of two-pulse 780-nm pump/1250-nm probe (solid curve) and three-pulse 780-nm pump/2000-nm re-pump/1250-nm probe (dashed curve) experiments on Na^- in THF. The 2000-nm pulse is applied at a delay of 5.8 ps (marked by arrow), acting primarily on solvent-separated contact pair electrons after the recombination of immediate pairs is complete. (b) Difference signals for the data in a (solid curve) and for separate experiments where the pump wavelength was 390 nm and the 2000-nm pulse arrived after ∼500 ps, acting primarily on the free electrons remaining after most solvent-separated pairs had recombined.

evident from the small negative offset due to enhanced recombination. The figure shows clearly that the bleach recovery of the free electrons is quite similar to that of the solvent-separated electrons, and both traces in Fig. 4b fit well to a single exponential decay with time constant ∼450 fs plus an offset (fits not shown in the figure for clarity). Together, these two traces suggest that the excited-state lifetimes of solvent-separated contact-pair electrons and free solvated electrons in THF are the same.

We are now in the position to ask whether or not the presence of a nearby sodium atom plays any significant role in the excited-state relaxation pro-

cess. The dashed curve and open circles in Fig. 5 show the ground-state absorption recovery for the solvent-separated and free solvated electrons, respectively. These data are the same as in Fig. 4b, but corrected for the change in recombination dynamics in a similar manner as described for the immediate contact pairs. Of course, the altered recombination dynamics for these long-lived species are constant on the ∼10-ps time scale considered here, so the correction procedure effectively removes only the long-time offset in the data, leaving an exponentially decaying trace with a ∼450-fs time constant. Fig. 5 also shows that within the experimental precision and the accuracy of the recombination correction procedure, the bleach recoveries of the solvent-separated and free electrons are identical to that of the immediate pair e_s^-: surprisingly, the solvated electrons in all three environments relax with the same ∼(450 fs)$^{-1}$ rate. This result implies that the sodium atom is not directly involved in the relaxation process of the electron in THF, strongly suggesting that the excited-state lifetime of the e_s^- is insensitive to the details of the specific atoms or molecules in the first solvent shell. This would be the case if the solvent motions that cause non-adiabatic coupling are not localized in the first solvent shell but instead are spread throughout the fluid, in accord with the theoretical predictions of Prezhdo and Rossky [14–16].

One caveat when considering the corrected data in Fig. 5 is the possibility that the ground state bleach recovery does not directly measure the excited-state lifetime but instead tracks solvation dynamics in the ground state subsequent to very fast internal conversion [4]. In previous work, however, we have shown that solvent relaxation processes do not strongly affect the absorption spectrum of solvated electrons in THF [24,26]; the breadth of the spectrum (cf. Fig. 1a), which results from the bound-to-continuum nature of the transition, makes the position of the electron's absorption highly insensitive to the local solvent environment. In addition, we also have performed three-pulse experiments probing at 490 nm, measuring the effects of the 2000-nm pulse on the amount of Na^- produced by the altered recombination dynamics [27,28]. We found that suppression of Na^- production by 2000-nm excitation of immediate contact pairs was not instantaneous; the time it takes to shut off the recombination, ∼450 fs, matches perfectly with the corrected bleach recovery data presented in Fig. 5 [28]. In combination, all the results suggest that the data in Fig. 5 do provide a direct measure of the electron's excited-state lifetime.

The fact that the lifetime of the e_s^- is the same in each of the three distinct environments that can be created by CTTS photodetachment from Na^- in THF has important implications for condensed-phase reaction dynamics. The excited state of the e_s^- in THF is delocalized throughout the fluid's conduction band; the solvent motions that cause non-adiabatic relaxation are those that localize the electron's wavefunction back into a local solvent cavity. For the photoexcitation of electrons in immediate or solvent-separated pairs, the excited-state wavefunction is large enough to completely encompass the nearby Na^0 [27,28]. The fact that the intimate presence of a sodium atom, which has a ∼0.5 eV binding affinity for the electron [35], makes no difference to the rate of non-adiabatic relaxation strongly indicates that non-adiabatic coupling is a collective solvent phenomenon. This implies that simple 'inner-sphere' ideas for electron transfer and similar condensed phase reactions do not provide a complete description of non-adiabatic coupling. Overall, based on the results presented here for charge transfer reactions, our experiments suggest that theories of non-adiabatic reactions in solution, including solvent effects on reaction rates, curve-crossings, or product branching ratios, need to account for how solvent motions far from a solute can affect the reaction dynamics.

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