

The roles of the solute and solvent cavities in charge-transfer-to-solvent dynamics: Ultrafast studies of potasside and sodide in diethyl ether

Molly C. Cavanagh, Ryan M. Young,^{a)} and Benjamin J. Schwartz^{b)}

*Department of Chemistry and Biochemistry, University of California,
Los Angeles, California 90095-1569, USA*

(Received 3 April 2008; accepted 12 August 2008; published online 2 October 2008)

Although electron transfer reactions are among the most fundamental in chemistry, it is still not clear how to isolate the roles of the solute and solvent in moving charge between reactants in solution. In this paper, we address this question by comparing the ultrafast charge-transfer-to-solvent (CTTS) dynamics of potasside (K^-) in diethyl ether (DEE) to those of sodide (Na^-) in both DEE and tetrahydrofuran (THF). We find that for sodide in both DEE and THF, CTTS excitation leads to delayed ejection of a solvated electron that appears with its equilibrium absorption spectrum. This indicates that the ejected electrons are localized in pre-existing solvent traps, suggesting that the structure of liquid DEE is characterized by cavities that are favorably polarized to localize an excess electron, as has been previously shown is the case for liquid THF. We also find that the geminate recombination dynamics following CTTS excitation of sodide in THF and DEE are similar, suggesting that the nature of the CTTS excited states and their coupling to the electronic states supported by the naturally occurring solvent cavities are similar in the two solvents. In contrast, the geminate recombination dynamics of potasside and sodide in DEE are different, with red-edge excitation of the K^- CTTS band producing a greater number of long-lived electrons than is seen following the corresponding red-edge excitation of the Na^- CTTS band. This indicates that the CTTS excited states of K^- are better able to couple to the electronic states supported by the naturally occurring solvent cavities, allowing us to compare the energetic positions of the potasside and sodide ground and CTTS excited states on a common absolute scale. Finally, we also observe a strong transient absorption following the CTTS excitation of potasside in DEE that correlates well with the 766 nm position of the gas-phase potassium D-line. The data indicate that CTTS excitation of alkali metal anions essentially instantaneously produces a gas-phase-like neutral alkali metal atom, which then spontaneously undergoes partial ejection of the remaining valence electron to form a neutral alkali metal cation:solvated electron tight-contact pair. © 2008 American Institute of Physics. [DOI: 10.1063/1.2977995]

I. INTRODUCTION

The fundamental step in almost all chemical reactions involves the transfer of electrons between reacting species. In solution, the dynamics of electron transfer is mediated by solvent motions that occur on ultrafast time scales. Understanding these fast motions is vitally important to understanding the role of the solvent in these chemical reactions. With most solutes, however, it is difficult to experimentally separate the roles of intramolecular degrees of freedom and the solvent in driving electron transfer.¹ Thus, it is desirable to isolate the role of the solvent motions coupled to charge transfer. The approach that we will take in this paper is to use atomic solutes to probe the solvent motions underlying electron transfer reactions. Since atoms have no internal degrees of freedom, any spectral dynamics observed during the course of electron transfer must directly reflect the motions of the solvent. Studies of atomic electron transfer reactions can provide clues not only about solvent dynamics but also

about solvent structure, since atomic chromophores serve as a direct probe of the local solvent environment.

Solvated atomic anions are particularly well suited for probing the role of the solvent in electron transfer. In the gas phase, atomic anions have no bound electronic excited states; optical excitation with sufficient energy can lead only to detachment of the excess electron. When an atomic anion is dissolved in solution, however, the solvent cavity surrounding the anion confines the excited electron, creating one or more bound excited states. The presence of these solvent-mediated bound excited states leads to an intense feature in the solvated anion's absorption spectrum known as a charge-transfer-to-solvent (CTTS) transition.²⁻²⁶ Excitation of an anion's CTTS transition detaches the electron from the atom, but the electron is still confined by repulsive interactions with the surrounding local solvent cavity. Solvent motions subsequent to the excitation then cause the electron to be ejected from the anion's cavity, producing a solvated neutral atom and a solvated electron.^{2-4,8,21} Thus, the CTTS dynamics of solvated atomic anions are those associated with the simplest possible electron transfer reactions, providing ideal systems in which to isolate the role of the solvent.

^{a)}Presently at Department of Chemistry, University of California, Berkeley.

^{b)}Electronic mail: schwartz@chem.ucla.edu.

To date, the most extensive studies of atomic anion CTTS dynamics have focused on either iodide (I^-) in water⁴⁻⁷ or sodide (Na^-) in tetrahydrofuran (THF),⁸⁻¹⁴ although a variety of other anion/solvent combinations also have been investigated.^{2,3,15-24} The information obtained in these studies has shed light on how both solvent structure and solvent motions dictate the CTTS mechanism. For example, CTTS electron ejection from sodide in THF (Refs. 8-14) has dynamics that are not only qualitatively different from those following CTTS electron ejection from aqueous iodide⁴⁻⁷ but also qualitatively different from those following CTTS excitation of iodide in THF.^{26,27} Do these different behaviors result from the different electronic structures of iodide and sodide or do they reflect a more fundamental difference in the solvent motions coupled to the CTTS dynamics of these solutes? Understanding these differences in CTTS dynamics is essential to isolating the role of the solvent in the CTTS process. In this paper, we address this question directly by studying the ultrafast CTTS dynamics of two solutes with nominally identical electronic structures: sodide (Na^-) and potasside (K^-). Comparing these two solutes allows us to look at how changing the local solvent environment without changing the long-range solvent structure affects the CTTS dynamics. We also use the CTTS dynamics of sodide and potasside in diethyl ether (DEE) to probe the structure of DEE and to infer that DEE, like THF, is a solvent that naturally contains many positively charged cavities located throughout its solvent structure.^{14,26,28-30}

The results we present in this paper show that sodide and potasside have similar CTTS ejection mechanisms, but with differences in recombination behavior that allow us to locate the position of the anion CTTS excited states relative to the solvent cavity-supported excited states. We also find that the spectral dynamics of the neutral atom left behind following CTTS ejection of the electron from the anion are quite similar for Na^- and K^- .^{13,14} Finally, for reasons described in the next section, we have carried out all these studies in DEE rather than THF. We find that the alkali CTTS ejection dynamics are nearly identical in DEE and THF,^{15,16} allowing us to infer properties of the structure and the nature of the cavities in liquid DEE.

II. EXPERIMENTAL DETAILS

Although the absorption spectrum of potasside in THF has been reported in the literature,³¹ (Fig. 1, thin dashed curve), we found that we could not prepare samples of potasside in THF at room temperature that were stable enough for pump-probe spectroscopy. It is for this reason that in this paper we compare the CTTS dynamics of sodide and potasside in DEE. We also compare the dynamics of sodide in DEE and THF.

Our solutions of sodide in THF were made following the procedure that we have published previously,¹⁴ which is a modification of the original work by Dye and co-workers.³²⁻³⁶ To prepare sodide solutions in DEE, we placed sodium metal (Sigma-Aldrich, used as received) as well as a small amount of potassium metal (Sigma-Aldrich, used as received), which is necessary to initiate the dissolu-

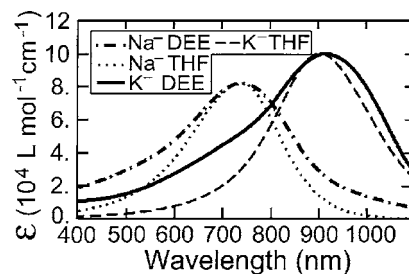


FIG. 1. Absorption spectra of alkali metal anion CTTS transitions in liquid THF and DEE: sodide (dot-dashed curve) and potasside (solid curve) in DEE, taken from experimental data, and sodide (dotted curve) and potasside (thin dashed curve) in THF, taken from fit parameters given in the literature (Ref. 31). The sodide and potasside spectra in DEE were scaled to have the same maximum absorbance as reported in THF.

tion of the sodium and is a potential source of potassium impurities, in an $\sim 1000:1$ by volume DEE/15-crown-5 ether solution to which a tiny amount of 18-crown-6 ether was added (also to aid initiation of the metal dissolution).¹⁶ We then sonicated this mixture until the characteristic dark blue color of sodide appeared. We made potasside/DEE solutions following the same procedure, except that we did not add sodium metal and we used larger amounts of 18-crown-6 ether in the preparation process. Figure 1 shows the absorption spectra of sodide (dash-dotted curve) and potasside (solid curve) in DEE as measured in our laboratory, as well as the absorption spectra of sodide (dotted curve) and potasside (thin-dashed curve) in THF taken from parameters given in the literature.³¹ Due to the limitations of the detector in our UV-visible spectrometer, we were only able to obtain the absorption spectra of our samples out to 1100 nm; however, we note that previous work has established that in ethers, sodide is the only absorbing species—solvated electrons do not exist at equilibrium in these solutions.^{8,32,33} Since we could not independently determine the anion concentration in the DEE solutions, we have plotted the absorption spectra in DEE assuming that the extinction coefficient at the absorption maximum in DEE is the same as that in THF. If the maximum extinction coefficient is the same in DEE as in THF, then the typical concentration of the samples used in our experiments varied between 0.02 and 0.2 mM.

Unfortunately, potassium metal is always contaminated with some amount of sodium, and it was necessary to use potassium metal in our sodide preparation process, so many of our samples were unstable. Often, we would see samples convert to mixtures with approximately equal amounts of sodide and potasside. For this reason, in all of the ultrafast work presented below, we were careful to use only samples that were stable in the sense that the relative amount of Na^- or K^- in each sample, as measured by UV-visible absorption, did not change during the course of the pump-probe experiments. With this safeguard, we found that even for samples with different overall concentrations (as well as for samples in which the total concentration decreased in time), the CTTS dynamics that we measured did not change within the 95% confidence limit, as determined by the variation across multiple scans (shown as the error bars presented in the figures below). We also found that the dynamics did not change when we varied the amount of crown ether in our sample

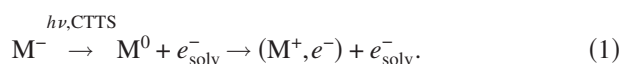
preparation process and that the dynamics did not change over time, even when samples were used for several days, suggesting that there was no significant buildup of photo-products affecting our dynamics. We also were careful to excite the sodide and potasside samples at wavelengths where only the anion of interest absorbs. Further details of our sample preparation process and how sample cross contamination restricted our choice of excitation wavelengths are presented in the supporting information.³⁷

The details of our single-wavelength femtosecond pump-probe spectrometer setup have been published previously.³⁸ Briefly, the experiments were done using a regeneratively amplified Ti:sapphire laser from Spectra Physics that produces pulses of ~ 120 fs duration at a 1 kHz repetition rate, with center wavelengths between 780 and 790 nm. A major fraction of the fundamental beam was directed into an optical parametric amplifier to create tunable signal and idler pulses in the ~ 1.1 – 2.4 μm region. For experiments utilizing ~ 790 or 395 nm excitation light, a small amount of the fundamental was either used directly or was frequency doubled in a beta-barium borate (BBO) crystal. For all the experiments, either the pump pulse or the probe pulse was directed onto a computer-controlled translation stage that produced a controlled variable time delay. A chopper was placed in the pump beam so that the signal could be measured alternately in the presence and the absence of the pump beam. A small portion of the probe beam was split off before the sample and sent to a reference detector, and the data were double normalized (signal versus reference and pump on versus pump off) on a shot-by-shot basis. All of the data were collected with the relative polarizations of the pump and probe beams set to the magic angle (54.7°) and all of the experiments were performed at room temperature. We performed pump-probe measurements at several excitation intensities to ensure that we were in a regime where the dynamics did not depend on excitation intensity and that there was no two-photon excitation of any of the alkali anions.¹¹ For experiments probing the dynamics of the ejected electrons at wavelengths near ~ 2 μm , we found the zero of time and instrumental response by measuring the cross correlation of the pump and probe pulses using either a BBO crystal or a Si wafer placed at the position of the sample for the THF experiments (see Figs. 4 and 5, below).

III. THE ULTRAFAST CTTS DYNAMICS OF SODIDE AND POTASSIDE IN DEE

A. The spectroscopy of the CTTS photoproducts of alkali anions in weakly polar ether solvents

Following CTTS excitation of an alkali metal anion (M^-) in solution, the photoproducts that are created are a solvated electron e^-_{solv} and a species whose stoichiometry is that of a neutral alkali metal atom (M^0),



For sodide in THF, experiments have shown that immediately following excitation, the metal atom that is left behind has a spectrum that resembles that of the Na 590 nm gas-phase D-line, although broadened and split by interactions

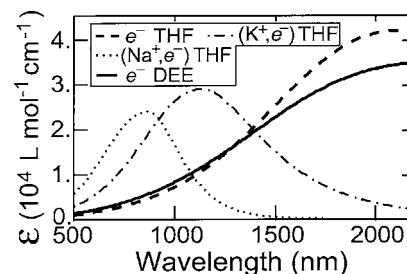


FIG. 2. Spectra of the solvated electron and the neutral alkali product species created following CTTS excitation of alkali metal anions in DEE and THF: the (Na^+, e^-) (dotted curve) and (K^+, e^-) (dot-dashed curve) tight-contact pairs in THF, taken from fit parameters given in the literature (Ref. 31); the spectra of these species in DEE have not been previously reported (Ref. 42). Also shown are the absorption spectra of the solvated electron in THF (dashed curve) and DEE (solid curve), reconstructed from spectral parameters given in the literature (Ref. 56).

with the local solvent environment.^{13,14} Subsequent solvent motions, which take place on an ~ 750 fs time scale, cause partial ejection of the remaining alkali atom valence electron, leading to formation of an unsolvated metal cation:electron tight-contact pair, (M^+, e^-) .^{13,14} The unsolvated contact pair then is solvated on a slow, ~ 5 – 10 ps, time scale.¹⁴ Figure 2 shows the known spectra of both the solvated (Na^+, e^-) (dotted curve) and solvated (K^+, e^-) (thin dot-dashed curve) alkali cation:solvated electron tight-contact pairs in THF.^{31,39–41} To the best of our knowledge, the spectra of the (Na^+, e^-) and (K^+, e^-) tight-contact pairs have not been observed previously in DEE,⁴² although indirect evidence for the formation of the (Na^+, e^-) species has been seen in ultrafast pump-probe experiments studying sodide CTTS dynamics in DEE.^{16,43} One of the goals of this work is to see if the potassium D-line can be observed near its gas-phase value of 766 nm (Ref. 44) following CTTS excitation of K^- , and if a similar partial ejection of the second electron takes place to form the (K^+, e^-) tight-contact pair. In addition to producing solvated metal atoms/metal cation:electron tight-contact pairs, CTTS excitation of alkali metal anions also produces solvated electrons. Although there is a significant amount of spectral overlap of the solvated electron with the alkali anion CTTS bands and the absorption of the various tight-contact pair species, the absorption spectra of solvated electrons in THF and DEE extend far enough into the IR that their dynamics can be probed cleanly in the ~ 2000 nm spectral region, where nothing else in the alkali anion CTTS systems absorbs. Thus the electron dynamics provide the cleanest probe of the CTTS ejection.

B. Dynamics of the solvated electrons ejected following the CTTS excitation of Na^- in DEE and THF and K^- in DEE

In previous work,^{14,26} we have argued that one of the main features driving the CTTS dynamics of both sodide and iodide in THF is liquid THF's highly unusual solvent structure. Simulations have shown^{28,29} and neutron diffraction experiments have verified³⁰ that neat THF naturally contains large cavities and that the electrostatic potential in these cavities is positive, so that these cavities act as pre-existing traps for a negatively charged excess electron. One experi-

mental signature we have attributed to the important role of cavities in THF is the fact that newly detached CTTS electrons appear with their equilibrium spectrum: The cavities act as pre-existing traps into which an electron can be ejected with little additional solvent relaxation required.^{14,26} Simulations show that the excited states of sodide in liquid THF can lie physically either entirely in the original ground-state cavity or be partially distributed between the original and one or more other cavities, a scenario that we labeled as “disjoint excited states.”^{28,45} This suggests that when a solute’s CTTS excited state is isoenergetic with many solvent disjoint states, the coupling between the CTTS excited states and the disjoint states can cause excited CTTS electrons to relocalize far from their parent atoms.²⁶ We believe that the lowest-energy CTTS excited state of sodide in THF lies below that of the lowest solvent-supported disjoint state,¹⁴ since excitation on the red side of the Na^- CTTS band, e.g., at 900 nm, leads only to local ejection,¹⁰ allowing all of the CTTS ejected electrons to undergo rapid, ~ 1 ps, geminate recombination. In contrast, the higher-energy CTTS states of sodide in THF are able to couple to disjoint states: When the excitation wavelength is tuned to the blue, e.g., to 395 nm, $\sim 60\%$ of the ejected electrons are ejected far enough away that they do not recombine on a subnanosecond time scale.¹⁰

What is the likelihood that solvents other than THF contain naturally occurring cavities? We expect that in any solvent that contains cavities and therefore disjoint states, the dynamics of an electron ejected in a CTTS process will appear at equilibrium after a delay, as has been seen previously in THF.^{14,26,29} In this section, we begin by comparing the dynamics of the solvated electron ejected following CTTS excitation of sodide in THF and DEE. We show that the CTTS-electron ejection time, lack of solvation, and short-time geminate recombination dynamics of sodide are virtually identical in DEE and THF. This suggests that liquid DEE, like liquid THF, has a solvent structure that is characterized by voids that serve as pre-existing electron traps, and that the energies and densities of the disjoint electronic states supported by these cavities are similar in the two solvents.⁴⁶ We then compare the CTTS dynamics of Na^- with K^- in DEE. We find that the electron ejection dynamics of the two anions are similar, but that (relative to the excitation wavelength) a significantly higher fraction of the K^- electrons do not undergo rapid geminate recombination. This suggests that the lowest-energy CTTS excited state of K^- lies above the lowest-energy solvent-supported disjoint state, allowing us to compare the CTTS ground and excited-state energies of Na^- and K^- in DEE on a common absolute scale.

1. Comparison of the CTTS electron dynamics of Na^- in DEE and THF: The nature of solvent-supported disjoint states in DEE

We begin by comparing the CTTS electron dynamics of sodide in DEE to the CTTS dynamics of sodide in THF. Figure 3 shows that the CTTS dynamics of Na^- in DEE has similar behavior to the CTTS dynamics of sodide in THF: Following both 395 nm (upper panel) and 785 nm (lower panel) CTTS excitations, the appearance of the solvated electron’s absorption in DEE is clearly delayed, as was previ-

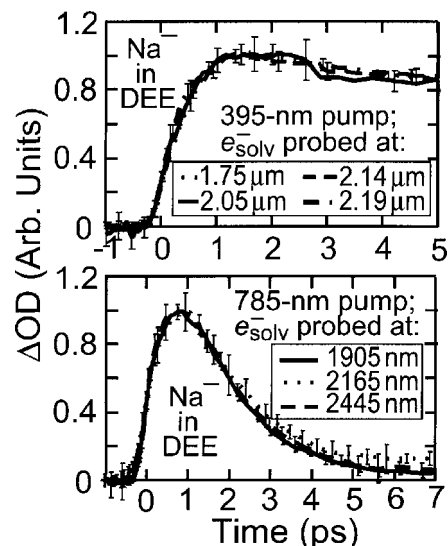


FIG. 3. Ultrafast spectral dynamics of the solvated electron ejected following both 395 nm (upper panel) and 785 nm (lower panel) CTTS excitations of Na^- in DEE. In both panels, the data are normalized at the maximum transient absorbance. The delayed rise and lack of solvation are consistent with the idea that DEE contains positively charged cavities, similar to what was observed previously for THF (Refs. 14 and 26).

ously observed in THF.^{8–10,14,16,47} Figure 3 also shows that the dynamics of the solvated electron are identical at probe wavelengths throughout the near IR where the solvated electron is the sole absorber (cf., Fig. 2), making it clear that there is no dynamic solvation of the electron after ejection. The upper panel shows that following high-energy excitation at 395 nm, only a small fraction of the CTTS-ejected electrons undergo geminate recombination with their partner sodium atoms, as evident from the small amount of decay of the electron’s absorption over the next few picoseconds. The lower panel of Fig. 3 shows that the amount of fast geminate recombination increases significantly when the excitation energy is lowered to 785 nm, similar to what we^{10,11,16} and others^{12,13} observed earlier for the CTTS dynamics of Na^- in THF.

Figures 4 and 5 show that the CTTS dynamics of sodide in DEE seen in Fig. 3 are not just similar to those of sodide in THF but are practically identical. Figure 4 makes clear

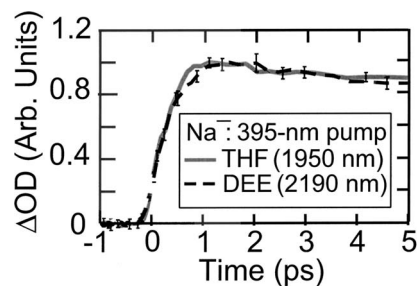


FIG. 4. Comparison of the ultrafast dynamics of the solvated electron ejected following the 395 nm CTTS excitation of sodide in THF (solid curve) and sodide in DEE (dashed curve). The two traces are normalized at the maximum transient absorbance, showing that for Na^- in these two solvents the amount of short-time electron recombination is the same. We note that there are some differences in the longer-time recombination dynamics (not shown here), which have been reported previously in the literature (Ref. 16).

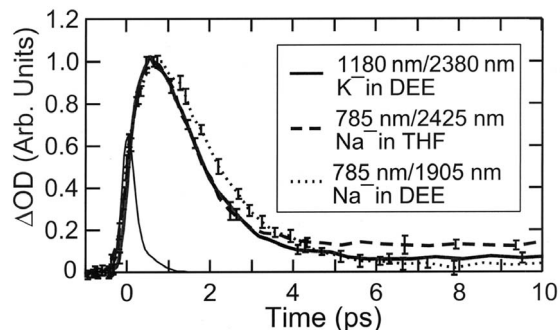


FIG. 5. Comparison of the ultrafast dynamics of the solvated electron ejected following CTTS excitation of sodide in DEE at 785 nm (dotted curve), sodide in THF at 785 nm (dashed curve), and potasside in DEE at 1180 nm (thick solid curve). All three traces are normalized at the maximum transient absorbance. The instrumental cross correlation of the 785 nm pump/2425 nm probe experiment is shown as the thin solid curve.

that following 395 nm CTTS excitation, both the delay time for appearance of the solvated electron's absorption and the amount and rate of geminate recombination on early time scales are identical within the noise for Na^- in THF (solid curve) and Na^- in DEE (dashed curve).⁴⁸ Figure 5 shows that the electron dynamics in DEE are also nearly identical to those in THF when exciting the low-energy side (785 nm) of the CTTS band. In both DEE and THF, electrons appear after a delayed rise followed by a fast (~ 1 ps) decay as nearly all the electrons recombine with their neutral sodium atom partners to reform sodide. The facts that the CTTS dynamics of sodide in DEE and THF are essentially identical (other than minor differences in the recombination time scales) following both 395 and 785 nm excitations and that there is no electron solvation (Fig. 3) provide strong evidence that DEE is like THF in that DEE contains cavities and disjoint states that can be accessed by CTTS-excited electrons.

We have argued in previous work that the fraction of electrons that do not undergo rapid geminate recombination following the CTTS excitation of anions in liquid THF is directly proportional to the density of solvent-supported disjoint states at the energy of the initially prepared CTTS excited state.^{14,26} Thus, the fact that the fraction of CTTS electrons ejected from Na^- that undergoes recombination is nearly identical in THF and DEE following both 395 nm (Fig. 4) and 785 nm excitation (Fig. 5) suggests that there is a similar density of disjoint states in DEE that lies at similar energies relative to the highest and lowest Na^- CTTS excited states. If the energies or density of the disjoint states in DEE relative to the sodide CTTS states were different from those in THF, we would expect to see dramatic differences in the geminate recombination behavior as a function of excitation wavelength in the two solvents. In fact, Fig. 5 shows that the fraction of long-lived electrons produced following 785 nm CTTS excitation of Na^- in DEE may be slightly lower than that in THF. This suggests that if anything, there is slightly less coupling between the low-lying sodide CTTS states and solvent disjoint states in DEE, so that relative to the Na^- CTTS states, the low-lying solvent-supported disjoint excited states in DEE lie at the same or possibly slightly higher energies as they do in THF.

2. Comparing the CTTS electron dynamics of Na^- and K^- in DEE

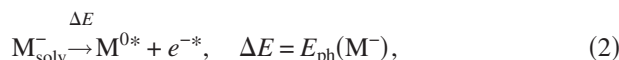
The similar CTTS behavior of sodide in THF and in DEE allows us to draw on our previous studies of the CTTS dynamics of Na^- in THF (Refs. 8–11, 14, and 16) to make meaningful comparisons between the CTTS dynamics of sodide and potasside in DEE. The thick solid curve in Fig. 5 shows the dynamics of the ejected electron following the 1180 nm CTTS excitation of K^- in DEE. This figure shows that the 1180 nm CTTS excitation of K^- in DEE leads to electron appearance dynamics that are nearly identical to those following the 785 nm CTTS excitation of Na^- in both DEE and THF. We also did experiments (not shown) where we excited the potasside CTTS band at 1180 nm and probed the potasside CTTS bleach at 590 nm. The rise of the bleach was instrument limited and the amount that the bleach recovered matched the amount of recombination seen in the decay of the electron's transient absorption, as expected. But, even though the *amount* of decay due to geminate recombination seen for the 1180 nm pump/590 nm probe is the same as that seen for the 1180 nm pump/electron probe for potasside in DEE, the decay time in the 590 nm probe bleach is faster than what was seen when probing the electron. This is likely due to the fact that the dynamics at 590 nm are due not only to the potasside bleach but also to the neutral potassium atom absorption at this wavelength.

The fact that the electron-ejection dynamics of potasside and sodide are so similar suggests that the mechanism for the CTTS electron to leave the initially prepared excited state and reach the ground state is similar for these two anions. For this low CTTS excitation energy, most of the electrons are ejected near the neutral potassium atom and recombine on a fast time scale. A small fraction of the excited electrons couple to disjoint states where we believe they nonadiabatically cascade through the solvent-supported disjoint states before relaxing into cavities far from the neutral potassium atom. These electrons recombine with their neutral potassium partners on a much slower time scale. Figure 5 verifies that the fast decay of the solvated electron's absorption due to geminate recombination is similar for K^- in DEE, Na^- in DEE, and Na^- in THF; the fact that the recombination of electrons ejected from sodide is slightly slower in DEE than THF has been noted previously in the literature.¹⁶ Thus, not only is the CTTS dynamics of sodide similar in DEE and THF but also the CTTS dynamics of K^- and Na^- in DEE are also very similar.

Although the CTTS electron ejection and recombination dynamics of sodide in THF and DEE and potasside in DEE look quite similar, there is one surprising aspect to the results shown in Fig. 5: The fraction of electrons that do *not* undergo rapid recombination, as measured by the height of the long-time absorption offset, is similar for sodide excited at 785 nm (in either solvent) and potasside excited at 1180 nm. The reason this is surprising is that the 785 nm excitation wavelength is close to the absorption maximum of the sodide CTTS band, but the 1180 nm excitation wavelength lies well to the red edge of the potasside CTTS absorption spectrum (cf. Fig. 1). In fact, the 1180 nm excitation wavelength lies at the same position relative to the K^- CTTS absorption maxi-

mum as 900 nm does for Na^- , and 900 nm is an excitation wavelength for which *all* of the CTTS-ejected electrons recombined with sodide (in THF) on the fast, ~ 1 ps time scale.¹⁰ The fact that no long-lived electrons were produced following 900 nm CTTS excitation of sodide in THF is what led us to argue in previous work that the lowest-energy CTTS state of sodide lies lower in energy than the lowest solvent-supported disjoint states in THF.^{14,26} Our observation that the equivalent far-red CTTS excitation of K^- produces long-lived electrons suggests that the lowest CTTS excited state of potasside in DEE can still couple to solvent disjoint states, which was not the case for Na^- in THF. Thus, given our argument above that the low-lying solvent-supported disjoint states lie at similar (or possibly slightly higher) energies in DEE relative to THF, the data in Fig. 5 indicate that the lowest CTTS state of K^- lies higher in energy than the lowest CTTS state of Na^- in DEE.

We can use the data in Fig. 5 to extract the relative solvation energies of the sodium and potassium anions in DEE. We start by defining the Franck–Condon alkali anion CTTS excitation process as



where M_{solv}^- is the equilibrated anion, M^{0*} is the weakly solvated gas-phase-like neutral alkali metal atom, e^{-*} is the excited CTTS electron at the instant of excitation, and $E_{\text{ph}}(M^-)$ is the photon energy required to reach the same absolute excited-state energy for each anion, which based on Fig. 5 we assume to be 1.05 eV (1180 nm) for potasside and 1.58 eV (785 nm) for sodide. It should be safe to assume that the solvation energies of Na^{0*} and K^{0*} are small given how similar the absorption spectra of these species are to the atomic gas-phase spectra, so any difference in the solvation energies of these gas-phase-like anions should also be small.⁴⁹ Putting these assumptions together with some simple thermodynamics gives

$$E_{\text{ph}}(\text{Na}^-) - E_{\text{ph}}(\text{K}^-) = -[E_a(\text{Na}) - E_a(\text{K}) + E_{\text{sol}}(\text{Na}^-) - E_{\text{sol}}(\text{K}^-)], \quad (3)$$

where $E_a(M)$ and $E_{\text{sol}}(M^-)$ are the gas-phase electron affinities and the solvation energies, respectively, of the M atoms and the M^- anions. Using the known 0.548 and 0.501 eV electron affinities of Na and K, respectively,⁵⁰ Equation (3) directly gives the difference in the solvation energies of sodide and potasside in DEE: $E_{\text{sol}}(\text{Na}^-) - E_{\text{sol}}(\text{K}^-) = -0.58$ eV. In other words, Na^- is solvated much better in DEE than is K^- . This result is consistent with what would be expected in THF, since sodide solutions are known to be more stable than potasside solutions, but this large stabilization of Na^- relative to K^- seems somewhat surprising in DEE. We know that DEE solutions of the two anions are roughly equally stable, as indicated by the fact that two anions can be prepared simultaneously in this solvent (cf. Sec. II and supplemental information³⁷), although part of the stability of these solutions may be due to large solvation energy differences or shifts in the binding equilibrium⁵¹ of the alkali cation/crown ether complexes.

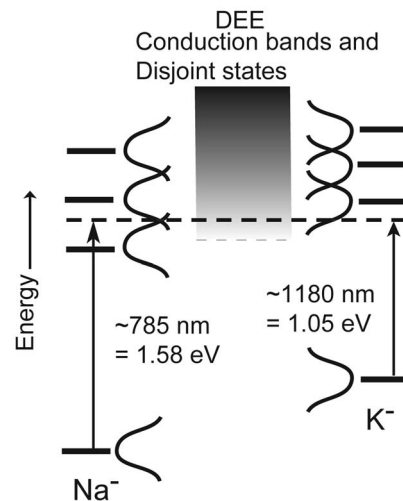


FIG. 6. Schematic of our understanding of how the energies of the Na^- and K^- ground and CTTS excited states (solid lines) lie relative to the solvent-supported disjoint states in DEE (gray-scale band with darker colors representing higher density of states). The ground state of K^- is drawn higher in energy than the ground state of Na^- both because the electron affinity of K is lower than that of Na and because K^- is less well solvated in DEE than Na^- (see text). The CTTS states of both Na^- and K^- are depicted as consisting of three CTTS excited states whose positions can be separated in polarized hole-burning experiments (Refs. 13 and 16). Based on the similar recombination dynamics seen in Fig. 5, we have drawn the 1180 nm excitation of K^- as accessing the same solvent disjoint states as the 785 nm excitation of Na^- (arrows and dashed line).

Figure 6 illustrates a schematic of our understanding of the energetics of the CTTS states of the alkali anions and the solvent-supported disjoint states in DEE based on the hypothesis that THF and DEE share similar disjoint states to which the CTTS excited states of the alkali anions can couple. We have assigned the CTTS band of sodide and potasside as arising from absorption from an s -like ground state to three CTTS excited states, which can be separated using polarized pump-probe experiments.^{13,16} Based on our previous observation that 100% of the ejected electrons undergo fast recombination following red-edge excitation of the Na^- CTTS band in THF (Ref. 10) and the fact that the wavelength-dependent recombination fraction is identical in THF and DEE (Figs. 4 and 5), we assign the lowest-energy CTTS band of sodide in DEE as lying below the energy of the lowest-available solvent-supported disjoint states. In contrast, the fact that some CTTS-ejected electrons escape recombination following low-energy excitation of potasside (Fig. 5) suggests that the lowest CTTS state of potasside in DEE does have some overlap with the lower-energy disjoint states of the solvent.

The fact that the Na^- and K^- anions in DEE have nearly identical CTTS electron kinetics for Na^- excited at 785 nm and K^- excited at 1180 nm strongly suggests that the CTTS excited states being accessed in these experiments are at the same absolute energy (as we have depicted in Fig. 6). It is possible, however, that the naturally occurring disjoint states in liquid DEE simply extend to lower energies than those in liquid THF, explaining why far-red excitation of sodide in THF led to 100% rapid recombination¹⁰ even though far-red excitation of potasside in DEE produced some long-lived solvated electrons (Fig. 5). We believe that this possibility is

unlikely, however, based on the recombination dynamics shown in Figs. 4 and 5. Although the recombination time scales are slightly different, the fraction of electrons that undergo rapid recombination is nearly identical for both the 395 and 785 nm excitation wavelengths for Na^- in both DEE and THF. This suggests identical overlap between the CTTS and disjoint excited states in both solvents at both high and low excitation energies. We also expect that the $\sim 0.5 \text{ \AA}$ size difference between potasside and sodide (see Table I, below) should have very little effect on the excited CTTS electron's ability to couple to the disjoint states since both simulations^{28,29} and experiments²⁶ suggest that the strongly coupled disjoint states are typically located several nanometers away from the original cavity. Therefore, we believe that the primary effect of changing anions is simply to provide an overall shift of the CTTS energy levels due to a change in the solvation energy, as depicted in Fig. 6; the positions of the solvent-supported disjoint states and their coupling to CTTS excited states are likely the same for both anions.

C. Dynamics of the neutral alkali species created via the CTTS excitation of Na^- and K^- in DEE

In addition to being able to easily monitor the dynamics of the ejected electrons and thus determine the relative energies of the alkali anion CTTS and solvent disjoint excited states, it also is possible to probe the dynamics of the neutral alkali species left behind during the CTTS process. As discussed above, the neutral Na atom that is left behind immediately following CTTS excitation of Na^- in THF has a strong absorption that is centered near 590 nm, the position of the D-line of the gas-phase Na atom.^{8,12–16} One of the goals of this study was to test the assignment of the 590 nm band as originating from the weakly solvated gas-phase-like sodium atom.^{13,14} If our understanding is correct, then we would expect to see a similar weakly solvated gas-phase-like absorption following the CTTS excitation of potasside near the position of the potassium D-line at 766 nm.⁴⁴

The lower panel of Fig. 7 shows the transient absorption dynamics of K^- in DEE excited at 1180 nm and probed near the potassium D-line wavelength using the laser fundamental at 785 nm. For comparison, the upper panel of this figure shows the results of a similar experiment in which we excited Na^- in DEE at 395 nm and probed near the position of the Na D-line at 580 nm. The data show that the transients are qualitatively (and nearly quantitatively) the same for sodide and potasside in DEE: Following CTTS excitation of both anions, the D-line dynamics shows the instrument-limited appearance of a transient absorption that crosses over into a net bleach after ~ 1 ps. Since both the sodide and potasside ground states should be strongly bleached at their respective D-line probe wavelengths, the presence of the early-time transient absorption suggests that the absorbing species created upon excitation has a very large cross section, consistent with assignment to a weakly perturbed alkali atom D-line.^{13,14} For both anions, the details of the dynamics probed in these experiments are complicated because the signal at these wavelengths consists of a combination of

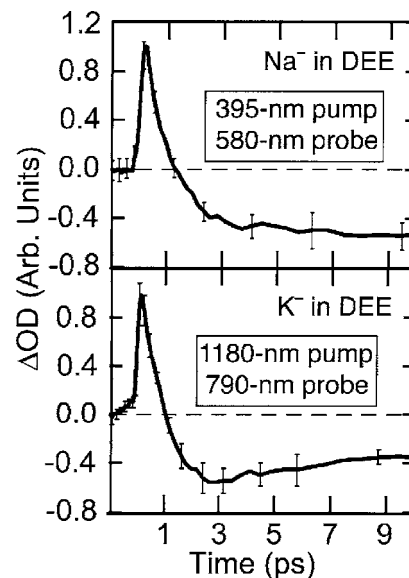


FIG. 7. Alkali atom D-line transient absorption dynamics following CTTS excitation of sodide at 395 nm (left panel, probed at 580 nm) and potasside at 1180 nm (right panel, probed at 785 nm) in DEE. The strong transient absorption at early times is assigned to the weakly solvated, gas-phase-like neutral alkali atoms that solvate and eventually react to become alkali cation:solvated electron tight-contact pairs, whose spectra are shown in Fig. 2.

ground-state bleach, solvated electron absorption, and neutral alkali atom absorption (cf., Fig. 1), of which the latter has complex dynamics due to its interconversion to form the alkali cation:solvated electron contact pair.^{13,14} Figure 7 suggests that in DEE, as was observed for sodide in THF, the electron and the alkali atom are no longer correlated immediately after excitation, as can be seen by the fact that the rise time of the solvated electron's absorption does not match the decay of the gas-phase-like atom's D-line. The fact that the transient absorption dynamics are so similar for these two anions, however, provides strong evidence that the primary product of the CTTS reaction of both Na^- and K^- in DEE really is a gas-phase-like neutral alkali metal atom and that the subsequent dynamics of the K atom (as well as that of the Na atom) in DEE are indeed similar to those previously investigated for sodide in THF.^{13,14}

Since alkali atoms have no internal degrees of freedom, the decay of the transient absorption seen in Fig. 7 must be due to motions of the solvent surrounding the gas-phase-like neutral atom that remains following CTTS excitation of the corresponding alkali anion. Immediately prior to the CTTS excitation, the solvent is configured into a polarized cavity in which the large parent anion resides; once the CTTS electron is ejected, however, the solvent must rearrange to optimally solvate the smaller neutral tight-contact pair. The greater the size and shape difference between the anion and the tight-contact pair, the more solvent reorganization must occur. For sodide in THF, we have argued that the ~ 700 fs decay of the D-line absorption is dominated by the time for the weakly solvated gas-phase-like species to react and become an *unsolvated* sodium cation:solvated electron tight-contact pair, a process presumably rate limited by the inward motion of solvent molecules from their original position around the anion to interact with the much smaller neutral species.¹⁴ Since

TABLE I. Calculated sizes of the alkali metal anions and neutral alkali cation:solvated electron tight-contact pairs in THF from spectral moment analysis using Eq. (4). The oscillator strengths were taken from the absorption spectra shown in Figs. 1 and 2 (Ref. 31). The size difference between Na^- and (Na^+, e^-) is the same as the size difference between K^- and the (K^+, e^-) , providing a reason why there are no qualitative differences in the decay of their D-line dynamics (Fig. 7).

M	M^- size (Å)	(M^+, e^-) size (Å)	Size diff. (Å)
Na	3.4	2.5	0.9
K	3.9	3.0	0.9
Rb	4.0	3.1	0.9
Cs	4.2	3.4	0.8

the potasside anion is quite a bit larger than the sodide anion, one might expect that the translational solvent motions associated with solvation of the neutral K species should be different from those for the neutral Na species following CTTS excitation of the corresponding anion. We can see from Fig. 7 that this is not the case: The relaxation time scales are the same for sodide and potasside. However, it is not simply the size of the ground state anion that dictates this time scale; instead, it is the difference in size and shape between the anion and the neutral tight-contact pair that should provide the driving force for the dominant solvent motions seen in the D-line transient absorption decay. Since the (Na^+, e^-) and (K^+, e^-) tight-contact pairs should have similar shapes, we expect that the time scale associated with the alkali atom D-line decay should be dominated by the change in size between the anion and the tight-contact pair.

To determine the size change that takes places following CTTS excitation, we used spectral moment analysis^{52,53} to determine the sizes of the sodium and potassium anions and the corresponding solvated cation:solvated electron tight-contact pairs. Moment analysis allows one to obtain the radius of an electronic species via a quantum mechanical expression that relates the size of an absorber to the negative-first moment of its experimentally measured oscillator strength,^{52,53}

$$\langle r^2 \rangle = \frac{3n_e \hbar \int_0^\infty \gamma(\omega) \omega^{-1} d\omega}{2m_e \int_0^\infty \gamma(\omega) d\omega}, \quad (4)$$

where $\sqrt{\langle r^2 \rangle}$ is the root-mean-square radius of the species being investigated, $\gamma(\omega)$ is the molar extinction coefficient of the species' absorption at frequency ω in units of $\text{M}^{-1} \text{cm}^{-1}$, m_e is the mass of the electron in kilograms, and n_e is the number of electrons involved in the optical transition (two for the anions and one for the alkali cation:solvated electron contact pairs).

Table I shows the sizes of Na^- , K^- and the (Na^+, e^-) and (K^+, e^-) neutral tight-contact pairs in THF calculated via Eq. (4) using the Gaussian–Lorentzian fits to the absorption spectra shown in Figs. 1 and 2.³¹ We chose to do the calculations for the THF-solvated species since the absorption spectra of the tight-contact pairs in DEE have not been previously reported. The table makes it evident that the size difference between the sodide anion and the neutral (Na^+, e^-) is the same as the size difference between the potasside anion and the neutral (K^+, e^-) , ~ 0.9 Å. Thus, the analysis in

Table I leads us to expect that the time for the solvent to rearrange from a structure optimized to solvate the anion to a structure optimized to solvate the tight-contact pair should be roughly the same following the CTTS excitation of sodide and potasside. This provides a simple explanation as to why the D-line transient absorption dynamics of Na^- and K^- seen in Fig. 7 are so similar. Interestingly, the moment analysis presented in Table I predicts that the size change following CTTS excitation of ceside (Cs^-) is a bit smaller than that of the other alkali anions, so the amount of solvent translation and presumably the D-line solvation time should be smaller as well. So far, our attempts to verify this prediction have met with little success because of the difficulty of preparing Cs^- samples that are stable enough for pump-probe experiments.

IV. CONCLUSIONS

In this paper, we have explored the nature of the CTTS dynamics of both sodide and potasside in DEE. We found that the electron ejection and recombinations dynamics following CTTS excitation of sodide in DEE are very similar to those in THF, which suggests that DEE, like THF, contains many positively charged cavities that support low-lying disjoint electronic states that can couple to CTTS excited states. The fact that the Na^- CTTS electron kinetics are essentially the same in both solvents for both blue and red excitation wavelengths (Figs. 3–5) suggests that the energetic position and density of the solvent-supported disjoint states are the same in both solvents. We also found that the dynamics of CTTS electron ejection and recombination of potasside in DEE are very similar to that of sodide in DEE. For the red-edge excitation of both K^- and Na^- , CTTS electron ejection is delayed, and a significant fraction of the ejected electrons undergo geminate recombination with their neutral alkali partners on a ~ 1 ps time scale. CTTS excitation of both K^- and Na^- leads to a very strong instantaneous transient absorption near the position of the atom's gas-phase D-line absorption, and the spectral dynamics of this D-line absorption is very similar for the two anions (Fig. 7). This provides strong evidence in support of the assignment that CTTS excitation of an alkali anion leaves behind a weakly solvated gas-phase-like neutral alkali atom.^{8,12–16} The one significant difference between the two anions, however, is in the fraction of CTTS-ejected electrons that do not undergo rapid geminate recombination: for sodide in THF, red-edge CTTS excitation at 900 nm causes *all* of the ejected electrons to undergo recombination within ~ 1 ps,¹⁰ whereas red-edge excitation of potasside in DEE at 1180 nm produces a significant number of long-lived electrons. This implies that the lowest CTTS excited state of K^- lies higher in energy relative to the solvent-supported disjoint states than does the lowest CTTS excited state of Na^- , an idea consistent with our analysis that Na^- is better solvated in DEE than K^- .

Given the difference in the amount of fast electron recombination of Na^- and K^- , it is interesting to compare the effect of changing the anion size for the alkali anions in DEE to that of the halides in water. Kloepper *et al.* saw a greater survival probability or smaller amount of geminate recombi-

nation, following CTTS excitation of bromide in water than they did for iodide in water.¹⁸ This observation that smaller ions lead to a greater CTTS escape probability is the exact opposite of what we observed for potasside and sodide in DEE. We believe the opposing trends are due to a difference in ejection and recombination mechanisms in both the anions and the solvents. As has been discussed above, the existence of cavities in THF and DEE that act as electron traps provides a unique mechanism for excited CTTS electrons to escape their parents via nonadiabatic coupling, leading to completely different recombination dynamics than what is observed in water. In addition, the symmetry of the orbital that the electron must return to in order to recombine is different for the halides and the alkali anions: The ground state of the alkalides is *s*-like while that of the halides is *p*-like. It is therefore not surprising that an *s*-like solvated electron would have very different recombination rates in these two systems: The change in symmetry required to recombine with a halogen does not need to take place for recombination with an alkali atom, so presumably a smaller solvent fluctuation can accomplish the reattachment.^{25,45}

We close by commenting further on the fact that the electron recombination times following red-edge CTTS excitation are different for sodide and potasside in DEE (Fig. 5). In previous work, we had assigned the faster recombination time for sodide in DEE versus THF as resulting from the slight polarity difference in the two solvents, which could potentially change the spatial overlap of the solvated electron with the nearby alkali atom.¹⁶ However, this idea is not consistent with the fact that electron recombination with (K^+, e^-) in DEE is slightly faster than that with (Na^+, e^-), since the (K^+, e^-) species is larger and should have better overlap with a nearby solvated electron. This suggests that the molecular solvation environment around potasside is different enough from that of sodide to affect the recombination dynamics in a way that we do not yet entirely understand. In contrast, the delayed appearance time and the lack of solvation of the CTTS-ejected electron are seen not only for sodide in DEE but also for all the anions we have studied in THF, including iodide.^{9,14,26,27} As discussed in Sec. III B, we believe that the electron appearance kinetics are a direct reflection of nonadiabatic coupling between the CTTS excited states and the disjoint excited states that are a consequence of the naturally occurring cavities in both of these solvents. Thus, our measurements strongly support the hypothesis that DEE has cavities similar to those already observed in THF;^{14,26,28-30} it would be interesting to look for the DEE cavities via neutron diffraction.^{30,54} It also would be interesting to explore electron solvation kinetics in a wide variety of solvents as a means to search for those that contain pre-existing cavities.⁴³ Of particular interest would be to study CTTS dynamics in THF:water mixtures, since neutron diffraction experiments suggest that for some mole ratios, the cavities in the mixture actually have the opposite polarity as those in neat THF.⁵⁴ We will report on the CTTS dynamics of iodide in such mixtures in upcoming work.⁵⁵

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. CHE-0603766. R.M.Y. was supported by the Arnold and Mabel Beckman foundation as a Beckman scholar. We would also like to thank Steve Bradforth and Tai-Jong Kang for helpful discussions and Art E. Bragg and Ross E. Larsen for helpful discussions and for a critical reading of the manuscript.

- ¹D. S. Larsen, K. Ohta, Q. H. Xu, M. Cyrier, and G. R. Fleming, *J. Chem. Phys.* **114**, 8008 (2001).
- ²X. Chen and S. E. Bradforth, *Annu. Rev. Phys. Chem.* **59**, 203 (2008).
- ³M. J. Blandamer and M. F. Fox, *Chem. Rev. (Washington, D.C.)* **70**, 59 (1970).
- ⁴J. A. Kloepfer, V. H. Vilchiz, V. A. Lenchenkov, and S. E. Bradforth, *Chem. Phys. Lett.* **298**, 120 (1998).
- ⁵J. A. Kloepfer, V. H. Vilchiz, V. A. Lenchenkov, A. C. Germaine, and S. E. Bradforth, *J. Chem. Phys.* **113**, 6288 (2000).
- ⁶V. H. Vilchiz, J. A. Kloepfer, A. C. Germaine, V. A. Lenchenkov, and S. E. Bradforth, *J. Phys. Chem. A* **105**, 1711 (2001).
- ⁷A. C. Moskun, S. E. Bradforth, J. Thogersen, and S. Keiding, *J. Phys. Chem. A* **110**, 10947 (2006).
- ⁸E. R. Barthel, I. B. Martini, and B. J. Schwartz, *J. Chem. Phys.* **112**, 9433 (2000).
- ⁹I. B. Martini and B. J. Schwartz, *J. Chem. Phys.* **121**, 374 (2004).
- ¹⁰E. R. Barthel and B. J. Schwartz, *Chem. Phys. Lett.* **375**, 435 (2003).
- ¹¹I. B. Martini, E. R. Barthel, and B. J. Schwartz, *J. Chem. Phys.* **113**, 11245 (2000).
- ¹²Z. H. Wang, O. Shoshana, B. X. Hou, and S. Ruhman, *J. Phys. Chem. A* **107**, 3009 (2003).
- ¹³O. Shoshana, J. L. P. Lustres, N. P. Ernsting, and S. Ruhman, *Phys. Chem. Chem. Phys.* **8**, 2599 (2006).
- ¹⁴M. C. Cavanagh, R. E. Larsen, and B. J. Schwartz, *J. Phys. Chem. A* **111**, 5144 (2007).
- ¹⁵E. R. Barthel, I. B. Martini, E. Keszei, and B. J. Schwartz, in *Ultrafast Phenomena XII*, edited by M. Murnane, N. Scherer, J. Miller, and A. Weiner (Springer-Verlag, Berlin, 2003), p. 459.
- ¹⁶E. R. Barthel, I. B. Martini, E. Keszei, and B. J. Schwartz, *J. Chem. Phys.* **118**, 5916 (2003).
- ¹⁷V. H. Vilchiz, X. Y. Chen, J. A. Kloepfer, and S. E. Bradforth, *Radiat. Phys. Chem.* **72**, 159 (2005).
- ¹⁸J. A. Kloepfer, V. H. Vilchiz, V. A. Lenchenkov, X. Y. Chen, and S. E. Bradforth, *J. Chem. Phys.* **117**, 766 (2002).
- ¹⁹N. Takahashi, K. Sakai, H. Tanida, and I. Watanabe, *Chem. Phys. Lett.* **246**, 183 (1995).
- ²⁰R. A. Crowell, R. Lian, I. A. Shkrob, D. M. Bartels, X. Y. Chen, and S. E. Bradforth, *J. Chem. Phys.* **120**, 11712 (2004).
- ²¹A. Iwata, N. Nakashima, M. Kusaba, Y. Izawa, and C. Yamanaka, *Chem. Phys. Lett.* **207**, 137 (1993).
- ²²R. Lian, D. A. Oulianov, R. A. Crowell, I. A. Shkrob, X. Y. Chen, and S. E. Bradforth, *J. Phys. Chem. A* **110**, 9071 (2006).
- ²³M. C. Sauer, I. A. Shkrob, R. Lian, R. A. Crowell, D. M. Bartels, X. Y. Chen, D. Suffern, and S. E. Bradforth, *J. Phys. Chem. A* **108**, 10414 (2004).
- ²⁴M. C. Sauer, R. A. Crowell, and I. A. Shkrob, *J. Phys. Chem. A* **108**, 5490 (2004).
- ²⁵C. J. Smallwood, W. B. Bosma, R. E. Larsen, and B. J. Schwartz, *J. Chem. Phys.* **119**, 11263 (2003).
- ²⁶A. E. Bragg and B. J. Schwartz, *J. Phys. Chem. B* **112**, 483 (2008).
- ²⁷A. E. Bragg and B. J. Schwartz, *J. Phys. Chem. A* **112**, 3530 (2008).
- ²⁸M. J. Bedard-Hearn, R. E. Larsen, and B. J. Schwartz, *J. Chem. Phys.* **122**, 134506 (2005).
- ²⁹M. J. Bedard-Hearn, R. E. Larsen, and B. J. Schwartz, *J. Chem. Phys.* **125**, 194509 (2006).
- ³⁰D. T. Bowron, J. L. Finney, and A. K. Soper, *J. Am. Chem. Soc.* **128**, 5119 (2006).
- ³¹W. A. Seddon, J. W. Fletcher, F. C. Sopchysyn, and E. B. Selkirk, *Can. J. Chem.* **57**, 1792 (1979).
- ³²M. T. Lok, J. L. Dye, and F. J. Tehan, *J. Phys. Chem.* **76**, 2975 (1972).
- ³³J. L. Dye, M. G. Debacker, and V. A. Niceley, *J. Am. Chem. Soc.* **92**, 5226 (1970).
- ³⁴J. L. Dye, *J. Phys. Chem.* **84**, 1084 (1980).

- ³⁵ J. L. Dye, *Angew. Chem., Int. Ed.* **18**, 587 (1979).
- ³⁶ J. L. Dye, *Prog. Inorg. Chem.* **32**, 327 (1984).
- ³⁷ See EPAPS Document No. E-JCPSA6-129-627836 for information about our sample preparation process and how we restricted our excitation wavelengths to ensure we were only investigating our anion of interest. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- ³⁸ T. Q. Nguyen, I. B. Martini, J. Liu, and B. J. Schwartz, *J. Phys. Chem. B* **104**, 237 (2000).
- ³⁹ W. A. Seddon, J. W. Fletcher, F. C. Sopcshyshyn, and R. Catterall, *Can. J. Chem.* **55**, 3356 (1977).
- ⁴⁰ B. Bockrath and L. M. Dorfman, *J. Phys. Chem.* **77**, 1002 (1973).
- ⁴¹ W. A. Seddon and J. W. Fletcher, *J. Phys. Chem.* **84**, 1104 (1980).
- ⁴² J. W. Fletcher and W. A. Seddon, *J. Phys. Chem.* **79**, 3055 (1975).
- ⁴³ M. C. Cavanagh and B. J. Schwartz (unpublished).
- ⁴⁴ *CRC Handbook of Chemistry and Physics*, 71st ed., edited by D. Lide (CRC, Boca Raton, FL, 1990), pp. 10-1–10-127.
- ⁴⁵ W. E. Glover, R. E. Larsen, and B. J. Schwartz, *J. Chem. Phys.* (in press).
- ⁴⁶ We will show in Ref. 43 that the density of disjoint states for other ethers, as measured by the amount of long-lived electrons after the CTTS excitation of sodide, is similar at high and low CTTS excitation energies but not at intermediate energies.
- ⁴⁷ We note that the rise time at some of the IR probe wavelengths is obscured by an instrument-limited absorption (see Refs. 12 and 16), which we have assigned as a transition between the lowest and the highest CTTS excited states.
- ⁴⁸ Although the amount of electrons that recombine on a short time scale is the same in DEE and THF, the long time recombination dynamics is faster in DEE than in THF, as previously seen in Ref. 16.
- ⁴⁹ If we do not assume that the solvation of Na^{0*} and K^{0*} were small, Eq. (3) becomes $E_{\text{ph}}(\text{Na}^-) - E_{\text{ph}}(\text{K}^-) = -[E_a(\text{Na}) - E_a(\text{K}) + E_{\text{sol}}(\text{Na}^-) - E_{\text{sol}}(\text{K}^-) - E_{\text{sol}}(\text{Na}^{0*}) + E_{\text{sol}}(\text{K}^{0*})]$, where $E_{\text{sol}}(\text{M}^{0*})$ is the solvation energy of the gas-phase-like sodium or potassium atom that is formed immediately after CTTS excitation.
- ⁵⁰ T. Miller, *CRC Handbook of Chemistry and Physics*, 71st ed. (CRC, Boca Raton, FL, 1990), pp. 10–180.
- ⁵¹ R. B. A. Z. C. Bradshaw, J. S. Izatt, and J. Hathaway, *Comprehensive Supramolecular Chemistry* (Pergamon, New York, 1996), Vol. 1, pp. 35–95.
- ⁵² D. M. Bartels, *J. Chem. Phys.* **115**, 4404 (2001).
- ⁵³ W. Marbach, A. N. Asaad, and P. Krebs, *J. Phys. Chem. A* **103**, 28 (1999).
- ⁵⁴ D. T. Bowron, J. L. Finney, and A. K. Soper, *J. Phys. Chem. B* **110**, 20235 (2006).
- ⁵⁵ A. E. Bragg and B. J. Schwartz (unpublished).
- ⁵⁶ F. Y. Jou and L. M. Dorfman, *J. Chem. Phys.* **58**, 4715 (1973).