

## Hydrated Electrons at the Water/Air Interface

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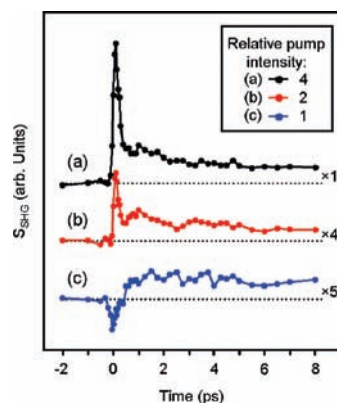
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When high-energy radiation passes through aqueous media, hydrated electrons are formed.<sup>1</sup> Such electrons, designated  $e^-_{(aq)}$ , are confined to cavities within liquid water. They are central to radiation chemistry and are important in fields as diverse as environmental chemistry, charge-induced reactivity, nuclear waste reprocessing, and biological radiation damage.<sup>2</sup> Since their discovery, their reactivity has been intensely studied in bulk water.<sup>3</sup> In reality, however, much of the reactivity of  $e^-_{(aq)}$  is expected to occur at interfaces of water with, for example, biological tissue or other low dielectric media. Our whole understanding of charged particles at interfaces has been transformed in recent years: the traditional view of the electrolyte–air interface as being devoid of ions has been replaced by a more nuanced picture in which certain ions can be strongly adsorbed even at interfaces with low dielectric media.<sup>4,5</sup> This then leads to the question of whether  $e^-_{(aq)}$ , the most fundamental of all anions, is attracted to such interfaces. In this communication, we investigate the solvation and dynamics of  $e^-_{(aq)}$  at the water/air interface.

Soft, polarizable anions that are weakly solvated tend to be adsorbed at the water/air surface, with the most dramatic enhancement shown by the iodide anion.<sup>5</sup> At the surface, the energy cost of disrupting the hydrogen bonded network is reduced, while solvation is maintained because of the large polarizability of  $I^-$ , allowing it to be asymmetrically solvated.<sup>5,6</sup> Hydrated electrons are also polarizable and structure-breaking, and it may be expected that  $e^-_{(aq)}$  would also be attracted to the surface. Evidence that surface-bound electrons exist has come from experiments on gas-phase clusters<sup>7,8</sup> and ice on metal surfaces<sup>9–11</sup> under ultrahigh vacuum conditions. Such experiments have attracted much recent interest, because of their relationship to  $e^-_{(aq)}$ . However, these are model surfaces where cold temperatures restrict the motion of the water molecules and the frozen local geometry provides stable potential wells in which the electron can reside. One unanswered question from the gas-phase cluster experiments is how these surface states evolve as the size of the nanocluster increases. Here, we investigate the planar water/air interface (the limit of infinite size) and show that, under ambient conditions,  $e^-_{(aq)}$  is fully hydrated and resides below the dividing surface.

As  $e^-_{(aq)}$  is a transient species, it must be created at a well-defined time. To achieve this experimentally, we used an  $\sim 120$  fs laser pulse centered at 250 nm to eject an electron from  $I^-$  ions adsorbed at the surface of a 2 M NaI solution, using its lowest charge-transfer-to-solvent (CTTS) absorption band. Although there is a slight red shift of the CTTS for surface-bound  $I^-$ , peaking at our pump wavelength,<sup>12</sup> the transition is sufficiently broad that a very large number of  $e^-_{(aq)}$  are concomitantly generated in the bulk. To discriminate against these bulk  $e^-_{(aq)}$ , the nonlinear spectroscopic method of second harmonic



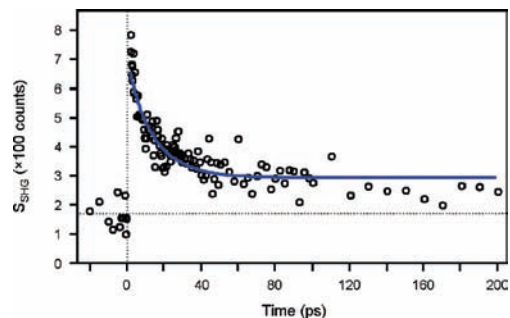
**Figure 1.** Transient SHG spectra measured at 700 nm at three decreasing pump intensities, (a) to (c) for a 2 M NaI solution. The signal at  $t < 0$  arises from the time-independent nonresonant response of the surface, as indicated by the dotted line; these are offset for clarity. The slow rise in SHG in (c) is assigned to the formation of interfacial hydrated electrons.

generation (SHG) is used.<sup>13</sup> Within the electric-dipole approximation, centrosymmetric media produce no SHG. This symmetry is necessarily broken at the interface between two media, and the SH generated from this interface allows for submonolayer sensitivity.<sup>14</sup>

The water surface gives an SHG signal even in the absence of  $e^-_{(aq)}$ , which arises from the nonresonant response of the water molecules and iodide ions. To distinguish the contribution of the  $e^-_{(aq)}$  from the nonresonant background, we choose a delayed femtosecond probe pulse centered at 1400 nm such that the SH wavelength is resonant with the well-known  $s \rightarrow p$  electronic transition of  $e^-_{(aq)}$ , which peaks at 720 nm in the bulk.<sup>1</sup> Experimentally, the SHG is measured in a reflection geometry and detected using a PMT based photon counter.

Figure 1a–c show three SHG transients with decreasing pump intensities. Figure 1a is characterized by a large peak immediately following CTTS, which decays on a subpicosecond time scale, and a slowly varying SHG signal beyond 1 ps. Reducing the pump power reveals that the large transient near time zero reduces in intensity relative to the SHG signal at longer times and, at very low pump energies, this feature has completely disappeared and is replaced by a negative going peak. Such signals are not uncommon in SHG experiments and arise from destructive interference between resonant and nonresonant contributions to the total observed signal.

The observation of a slow rise in the SHG signal to a maximum at  $\sim 1$  ps in Figure 1c is consistent with the initial solvation dynamics of  $e^-_{(aq)}$  observed in bulk transient absorption experiments<sup>15</sup> and in gas-phase cluster experiments.<sup>16</sup> In the bulk, the dynamics reflect the solvation of the electron and the

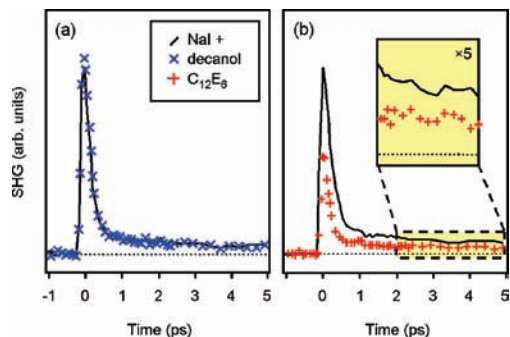


**Figure 2.** SHG signal (number of photons) as a function of pump–probe delay, showing the long-time relaxation dynamics of hydrated electrons at the interface. Horizontal dotted line indicates the nonresonant background. Blue line is a fit to a kinetic model. Data were collected out to 750 ps (long time data not shown).

neutral iodine atom as a contact pair. Transient absorption spectra show that the solvation process is characterized by a rapid blue shift of the absorption spectrum, which converges to that of  $e^-_{(aq)}$  after 1 ps. In the current experiments, the probe wavelength is fixed and the  $s \rightarrow p$  transition of  $e^-_{(aq)}$  becomes resonant with the second harmonic of the probe as the solvation occurs. This leads to a rise in the observed SHG signal as seen in Figure 1c. The SHG signal levels off after 1 ps as the absorption spectrum has converged to that of  $e^-_{(aq)}$  in the bulk. The increase in SHG is also present in Figure 1a and b but is obscured by the large feature near zero delay.

The large feature near  $t = 0$  arises from a higher order nonlinear excitation process, as indicated by its pump–power dependence shown in Figure 1. We tentatively assign this feature to two-photon absorption of interfacial iodide, resonance-enhanced by the CTTS and ultimately leading to highly excited states in the conduction band of water. These states are delocalized over many water molecules and are expected to exhibit a very large SHG response, as evidenced by the prominence of this feature at early times. However, these states do not produce a significant number of solvated electrons that are observed in our SHG experiments beyond the rapid decay of the feature (past the first few ps), suggesting that this is a minor ionization channel, relative to the CTTS channel. The origin of the transient feature near  $t = 0$  is considered in further detail in the Supporting Information.

The dynamics of the interfacial  $e^-_{(aq)}$  following initial localization are followed for 750 ps, and the first 200 ps are shown in Figure 2. At first glance, the dynamics appear qualitatively very similar to those observed for bulk  $e^-_{(aq)}$  using transient absorption.<sup>17</sup> Following the initial formation of a solvated contact pair of the neutral iodine and electron in  $\sim 1$  ps, this contact pair may then decay through nonadiabatic recombination to reform  $I^-$  or it may dissociate to form  $e^-_{(aq)}$  and iodine which then diffuse apart. In the condensed phase, these two competing processes occur on a 33 and 70 ps time scale, respectively.<sup>17</sup> The SHG data have been fit to this kinetic model and are shown in Figure 2. The qualitative agreement of the fit suggests that similar dynamics are occurring at the interface. A quantitative analysis requires the knowledge of the relative phases of the resonant and nonresonant contributions to the total signal, as described in the Supporting Information. Such experiments are currently underway in our laboratory. After



**Figure 3.** Dynamics of the hydrated electron following CTTS of a 2 M NaI solution (black line) and the relative effect on the dynamics following the addition of the surfactants (a) 1-decanol and (b)  $C_{12}E_6$ . Inset in (b) highlights the change in SHG signal arising from the hydrated electron due to the  $C_{12}E_6$ . The dotted line represents the nonresonant background.

all contact pairs have decayed, interfacial hydrated electrons can be observed for the duration of the experiment (up to 750 ps).

Gibbs defined the dividing surface between water and air as the plane for which the surface excess of water is zero. The “surface” that gives rise to SHG, however, is not a mathematical plane but is a region of finite thickness where the structure differs from the bulk phases on either side. The interfacial region just below the dividing surface may also contribute to the SHG because of the asymmetric environment at the electrolyte interface: the strong electric field generated by the separation of  $I^-$  and  $Na^+$  ions can distort the electron distribution and lead to electric-field induced SHG. Conceptually, we can consider two different interfacial locations for  $e^-_{(aq)}$ : the electron may be partially hydrated and sit at the dividing surface with some electron density exposed to the vapor phase (as seen in clusters and on ice surfaces), or it may be fully hydrated and localized just below the surface. To distinguish between these possibilities, we specifically modified the surface using two different nonionic surfactants: 1-decanol and hexaethyleneglycol dodecyl ether ( $C_{12}E_6$ ).

Decanol forms a liquid-like monolayer on the surface of water;<sup>18</sup> the OH group of the decanol does not penetrate into the aqueous phase. The hydrophobic chains extend away from the water and therefore significantly alter the local environment on the vapor side of the interface. The absorption spectrum of a solvated electron is sensitive to its local environment. For an electron bound at the dividing surface with some electron density outside the water, one would expect to observe changes in the SHG with decanol adsorbed. However, Figure 3a shows no detectable change demonstrating that the observed signals do not arise from surface-bound electrons.

In contrast,  $C_{12}E_6$  has a large polar headgroup comprising six ethylene glycol units that extends 1–2 nm into the water.<sup>19</sup> Its addition may be expected to affect the concentration profile of  $e^-_{(aq)}$  and iodide as well as their respective absorption spectra. Any of these perturbations will lead to changes in the observed SHG from the  $e^-_{(aq)}$  and would thus provide evidence that the SHG is generated from this interfacial region. Figure 3b shows that the addition of  $C_{12}E_6$  reduces the SHG arising from  $e^-_{(aq)}$ ; as shown in the inset, the SHG signal after 1 ps is reduced by a factor of approximately 2. This observation, together with the decanol data, shows that the electron is

localized within the interfacial region below the dividing surface. Importantly, it also eliminates the possibility that the observed SHG signal has come from the bulk through nondipolar interactions with the probe field since such a bulk signal would be insensitive to the very low concentration of  $C_{12}E_6$  in the bulk solution ( $\sim 0.25$  mM).

In the salt solution, the  $Na^+$  and  $I^-$  are on average only  $\sim 0.4$  nm apart according to molecular dynamics simulations;<sup>5</sup> beyond this the bipolar structure is lost within 1 nm. These simulations provide an approximate maximum depth from which SHG can be observed. The radius of gyration of  $e^-_{(aq)}$  in the bulk is  $\sim 0.24$  nm, and it has  $\sim 6$  water molecules in its first solvation shell.<sup>20</sup> Therefore, despite the apparent full solvation of the  $e^-_{(aq)}$ , it remains very close to the water/air dividing surface.

Our conclusion concerning the interfacial localization of the hydrated electron is supported by the similarity of the dynamics of the interfacial and bulk  $e^-_{(aq)}$ , as shown in Figure 2. However, it contrasts with deductions from gas-phase cluster and ice–metal surface experiments. These indicate that distinctive surface-bound electrons can be formed, albeit under cold conditions, and are stable for many microseconds. Our conclusion is consistent with molecular dynamics simulations,<sup>21</sup> which suggest that an electron initially bound to the surface of liquid water under ambient conditions prefers internal solvation. Calculations of the CTTS state of  $I^-$  at the water/air interface show that the electron density points toward the solvent,<sup>22</sup> so it is plausible that the ensuing dynamics should involve full solvation. In recent years, gas-phase cluster data have been critically scrutinized because they have not provided conclusive evidence about which, if any, of the experimentally observed isomers correlates to the bulk  $e^-_{(aq)}$ .<sup>23</sup> Our results suggest that many of the characteristics of an electron localized close to the dividing surface are shared with those of the bulk  $e^-_{(aq)}$ . These similarities may provide some insight into the apparent correspondence of the anionic water cluster isomer which is dominant under warm conditions with that of the fully hydrated electron.

The observation that  $e^-_{(aq)}$  remains at the interface for more than 750 ps suggests that it is sufficiently stable to be an important reagent at the water/air interface and at other interfaces, such as decanol, which can be viewed as a crude analogue of a biological membrane. For instance, a low-energy electron can induce single and double strand breaks in DNA.<sup>24</sup> Since much radiation damage originating from  $e^-_{(aq)}$  occurs at water interfaces,<sup>2</sup> our results present an important step toward the study of  $e^-_{(aq)}$  at interfaces pertinent to chemistry and biology.

**Note Added in Proof.** Since the submission of this communication, two papers describing photoelectron spectroscopy experiments

on liquid microjets have appeared.<sup>25,26</sup> Both report that the vertical binding energy of the hydrated electron is 3.3 eV. One also shows evidence of surface-bound electrons following two-photon ionization of pure water.<sup>25</sup> Such surface electrons were not detected in our experiments using CTTS transitions in iodide. Microjet experiments using CTTS from  $I^-$  or SHG experiments following two-photon ionization of pure water might resolve this discrepancy.

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**Supporting Information Available:** Experimental methodology; data analysis; description of nonlinear feature at zero delay; full ref 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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