Charge Transfer to Solvent Dynamics at the Ambient Water/Air Interface

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Supporting Information

ABSTRACT: Electron-transfer reactions at ambient aqueous interfaces represent one of the most fundamental and ubiquitous chemical reactions. Here the dynamics of the charge transfer to solvent (CTTS) reaction from iodide was probed at the ambient water/air interface by phase-sensitive transient second-harmonic generation. Using the three allowed polarization combinations, distinctive dynamics assigned to the CTTS state evolution and to the subsequent solvating electron-iodine contact pair have been resolved. The CTTS state is asymmetrically solvated in the plane of the surface, while the subsequent electron solvation dynamics are very similar to those observed in the bulk, although slightly faster. Between 3 and 30 ps, a small phase shift distinguishes an electron bound in a contact pair with iodine and a free hydrated electron at the water/air interface. Our results suggest that the hydrated electron is fully solvated in a region of reduced water density at the interface.

Electron-transfer reactions in aqueous solution represent one of the most fundamental chemical processes with broad importance in fields such as chemical biology, electrochemistry, radiation chemistry, and atmospheric chemistry. Of these reactions, the charge transfer to solvent (CTTS) reaction from a solute anion has been a prototype: It provides a unique opportunity to probe the initial dynamics of the surrounding water molecules as they reorient on an ultrafast time scale to solvate the new charge distribution, eventually forming a hydrated electron, $e^{-}(aq)$. A particularly useful means of initiating CTTS reactions is photoexcitation to CTTS absorption bands of certain aqueous anions. The most studied of these has been the CTTS of iodide, and a schematic of the solvation dynamics is shown in Figure 1. However, these studies have focused on the bulk dynamics, while arguably, electron-transfer reactions are of most interest at interfaces, be it on an aerosol particle, on an interstellar dust-grain, or at a water/biomolecule interface. In an attempt to probe interfacial CTTS dynamics of iodide, time-resolved photoelectron spectroscopy coupled to the liquid microjet technique has recently been used. Results from such experiments showed that the observable dynamics are very similar to those seen in the bulk. However, questions remain about that method’s surface sensitivity, which is governed by the photoelectron’s inelastic mean free path in the microjet, and about the nature of the surface at the vacuum/water interface in a liquid microjet. The only measurement of CTTS dynamics at an ambient water/air interface was performed using time-resolved second-harmonic generation (SHG) spectroscopy, which is surface sensitive by virtue of the second-order nonlinear nature of the SHG interaction, with the surface sensitivity defined by the depth over which inversion symmetry is broken. This experiment also showed dynamics similar to those observed in the bulk, suggesting very little influence of the surface on the observable dynamics, but suffered from complications arising from the nonlinear nature of the experiment. Here we overcome these limitations and revisit the dynamics of the CTTS reaction from iodide at the ambient water/air interface using a phase-sensitive time-resolved SHG experiment and show, using different symmetry-allowed polarization combinations, that distinctive surface solvation dynamics can be seen at the interface.

Experimentally, a 250 nm femtosecond pump pulse was used to initiate the CTTS process in a 2 M aqueous solution of NaI. As iodide partitions to both the bulk and the surface of water, the CTTS dynamics will be initiated at the water/air surface and in the bulk. To probe only the water/air interface, we employ phase-sensitive SHG. Phase-sensitive SHG has been used both nonspectroscopically and spectroscopically, and recently, a number of groups have combined this into time-resolved and phase-sensitive SHG, primarily for use at semiconductor interfaces. We have developed a variant of these techniques that is not spectroscopic but benefits from a lock-in measurement and excellent phase stability, which is crucial to the current measurements. The time-resolution of the experiment is ~100 fs.

Figure 2 shows contour plots of the amplitude of the phase- and time-resolved SHG for the three symmetry-allowed

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polarization combinations at two different fundamental wavelengths (1320 and 800 nm). The allowed polarization combinations are PP, PS, and Smix, where the first letter denotes the polarization of the SHG light and the second denotes the polarization of the fundamental light; mix refers to a mixture between S and P polarizations. The data have been fitted globally (see supporting materials) to recover the contributions of all transitions. An observed temporal phase shift can arise for two reasons: either a specific transition is exactly resonant with either the fundamental or its SHG. In principle, both the fundamental and probe wavelengths. For the 1320 nm probe, a significant portion of the signal decays within the first few picoseconds, while for the 800 nm probe the majority of signal remains. At both probe wavelengths, the PS combination has a greater relative long-term offset than PP.

In addition to the amplitude differences, clear differences in the phase dynamics can be seen. Specifically, in the Smix polarization combination, the phase changes by \( \sim \pi/2 \) over the first picosecond, while the other polarization combinations show comparatively small phase changes over longer time scales. The only exception to this is a very fast (sub-100 fs) phase shift near \( t = 0 \) in the PS polarization combination with an 800 nm probe.

The amplitudes, \( N(t) \), have been fitted to a simple kinetic model

\[
N(t) = g(t) \times \{ A \exp(-t/t) + B \}
\]

where \( A \) and \( B \) are constants, \( t \) is a time constant, and \( g(t) \) is a Gaussian instrument response function that has then been convoluted with the exponential decay. The model assumes that the initial signal decays according to first-order kinetics into a long-lived product that has a signal level of \( B \), and this subsequently decays on a time scale beyond the measurements. For PP and PS polarizations, where there are only small phase shifts, we fit only the amplitude to this model, while for Smix we additionally fit the phase to the model but exclude the convolutions with \( g(t) \) and any signal before \( t = 0 \) for this. The lifetimes determined from the fits are given in Table 1.

Although the focus of this work is on the initial solvation dynamics, additional phase-resolved measurements up to 100 ps using 1320 nm probe and the PP polarization combination were performed, and the results are shown in Figure 3. After the initial fast decay of the amplitude, there is a slow decay of the overall signal leaving a constant background at 100 ps. The kinetics have been fitted to a model proposed by Staib and Borgis,\(^{25}\) and this yields two lifetimes of 23 ± 4 and 54 ± 13 ps. The context of the fit and these lifetimes will be discussed below.

The intensity of the transient SHG signal is largely determined by the resonance-enhancement of the probe fundamental or its SHG. In principle, both the fundamental and SHG can be resonant. Transient absorption spectroscopy of the CTTS reaction from \( \Gamma^- \) in the bulk (excited at 242 nm) showed that the absorption spectrum rapidly blue-shifts from the IR to the visible on a 0.7 ps time scale (see Figure 1).\(^4\) The final spectrum peaks at \( \sim 720 \) nm and corresponds to the formation of the \([P^0:e^-]_{aq}\) contact pair. The 0.7 ps lifetime has been assigned to the reorganization dynamics of the water molecules to accommodate the new charge distribution. However, these lifetimes are derived from simple fits at a given probe energy, while the transient absorption is better described by a continuously shifting absorption spectrum. Therefore, a direct comparison between the lifetimes from our experiment and the transient absorption spectra is mostly qualitative. Additionally, transient fluorescence up-conversion showed that the initially excited CTTS state fluoresces over a broad spectral range spanning 300–700 nm (see Figure 1). The
broad emission reflects the inhomogeneous environments present as the CTTS is excited, and these lead to different dynamics, with the shorter wavelengths showing shorter lifetimes.26 Because of the very large spectral widths associated with the transient absorption of the solvating $[I_0:e^-]_{aq}$, and with the emission of the CTTS state, it is nearly impossible to quantitatively disentangle which steps in the SHG are resonant. However, we can use the known bulk energetics, time scales, and phase changes to disentangle the dynamics.

On the whole, the amplitude time-constants for the PP and PS data sets are close to, albeit slightly faster, than the 0.7 ps time scale attributed to the equilibration of the solvent surrounding the $[I_0:e^-]_{aq}$ contact pair in the bulk.4 The 1320 nm PP and PS data show that the initial signal is significantly larger relative to the signal after 3 ps compared with the same polarization combinations at 800 nm. This is consistent with the rapidly blue-shifting absorption spectrum of the $[I:e^-]_{aq}$ as it solvates because 1320 nm is more resonant.

Table 1. Fitted Time Constants

<table>
<thead>
<tr>
<th>polarization</th>
<th>$\tau$ (1320 nm)/ps</th>
<th>$\tau$ (800 nm)/ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>0.50 ± 0.02</td>
<td>0.48 ± 0.03</td>
</tr>
<tr>
<td>PS</td>
<td>0.67 ± 0.06</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>Smix (amplitude)</td>
<td>0.16 ± 0.01</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td>Smix (phase)</td>
<td>0.46 ± 0.04</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

“Uncertainties are obtained from the fitting procedure, although we believe they are an underestimate of the real uncertainty in the time constants. For Smix at 800 nm we present an estimate rather than a fit to the phase kinetics.

Figure 2. Kinetics of the CTTS solvation dynamics at a variety of polarizations and wavelengths. Dynamics with (a–c) an 800 nm probe (400 nm SHG) and (d–f) a 1320 nm probe (660 nm SHG). Different polarization combinations are shown in rows: PP in panels a and d, PS in panels b and e, and Smix in panels c and f. The contour plot shows the signal from the lock-in measurement as a function of stage position ($L$ (cm), top axis), with the corresponding absolute phase on the bottom axis (black dashed line; red dashed line is phase $\pm \pi$). The left-hand side of each plot shows the amplitude of the signal. The vertical axis corresponds to the delay between the CTTS excitation pulse and the probe.
In contrast with the PP and PS polarization combinations, the Smix data at both wavelengths show much faster amplitude kinetics as well as large phase changes on similarly fast time scales. The lifetime for these kinetics and phase changes is comparable to the ~0.2 ps suggested for the decay of the CTTS state to form the nonequilibrated \([I^0:e^−]_{(aq)}\) contact pair and is consistent with the time scales reported from the transient fluorescence up-conversion measurements. Therefore, it appears that the Smix polarization is more sensitive to the CTTS state dynamics rather than the initial solvation of the nonequilibrated \([I^0:e^−]_{(aq)}\) as seen for PP and PS. The SHG process from the CTTS state is shown pictorially in Figure 4a. While the solvating contact pair is in its electronic ground states, the CTTS state is an excited electronic state with \(I^−\) as the ground electronic state, as evidenced by the fluorescence spanning 300–700 nm from the CTTS state. Thus, the primary resonance that contributes to the kinetics at early times in the Smix polarization is between the occupied CTTS state and the \(I^−\) ground state. Crucially, only the SHG is resonant. To our knowledge, the CTTS state does not appear in transient absorption spectra with the current probe photon energies. The CTTS then evolves and undergoes a nonadiabatic transition to form the nonequilibrum \([I^0:e^−]_{(aq)}\), at which point the SHG signal is once again dominated by the absorption of the solvating \([I^0:e^−]_{(aq)}\). The large phase shift observed in Smix is likely related to the rapid decay of the CTTS state, as suggested in Figure 4a. Qualitatively, the initial phases at both probe wavelengths are consistent with the real part of \(\chi^{(2)}\) being of different sign at either side of the emission band so that at 400 nm it is closer to \(−\pi\) while at 660 it is closer to 0. The faster phase dynamics observed at 400 nm than at 660 nm SHG output is also consistent with the transient fluorescence that showed more rapid dynamics at shorter wavelengths.

A most striking point is that only the Smix appears to be sensitive to the CTTS state. Although Smix, PP, and PS probe different components of the \(\chi^{(2)}\) tensor, the main difference between Smix and PP or PS is the output polarization. We have argued that resonance with the second harmonic of the Smix data is mostly responsible for the dynamics observed over the first few 100 fs. Therefore, it appears that the resonant CTTS transition at the interface has a transition dipole moment predominantly aligned along the surface plane; otherwise, both PP and PS would also reveal dynamics associated with the CTTS state. In principle, the PP polarization combination also contains contributions from the same \(\chi^{(2)}\) component probed by Smix. However, we expect this to be relatively small because of the large angle of incidence used in the current experiment such that the response in PP is dominated by components normal to the surface, and thus only \([I^0:e^−]_{(aq)}\) is probed.

Bradforth and Jungwirth have calculated the electronic structure of the CTTS state of \(I^−\) at a water/vacuum interface and concluded that its orbital points toward the solvent (not the vacuum) as it initially occupies a preformed void next to the iodine. The calculated orbital is highly asymmetric. According to their calculations, the orbital is of mixed character: predominantly s- with additional p-character. A radial node exists between the iodine and the extruding diffuse lobe of the CTTS state, which has also been seen in previous simulations. As shown in Figure 4b, the resonant transition for the SHG in the S-polarized output arises from the transition moment that couples this CTTS back to the \(\Gamma \cdot (5p)\) states. For the CTTS state to only be observable by the Smix polarization, therefore, requires that there is a preferential alignment of the electron.

**Figure 3.** Kinetics over the first 100 ps following CTTS excitation. Plot shows the same information as Figure 1 but over an extended time scale. The dynamics were probed with PP polarization combination and at 1320 nm (660 nm SHG). The amplitude has been scaled by a factor of 5 to highlight the decay after the initial fast kinetics. The solid black line through this is the fit to the kinetics.

**Figure 4.** Schematic of transitions leading the SHG and the surface CTTS reaction. (a) The initial CTTS state SHG response involves primarily "emission" transitions from the CTTS state to \(I^−\) that are resonance with the second harmonic of the probes. The SHG response of the presolvated \([I^0:e^−]_{(aq)}\) contact pair is initially dominated by "absorption" transitions with the fundamental at 1320 nm and to a lesser extent 800 nm. Equilibrated \([I^0:e^−]_{(aq)}\) is probed by transitions as shown. (b) Photoexcitation produces a CTTS state that is predominantly aligned in the plane of the interface so that transitions that are S-polarized (double arrow) predominantly probe this CTTS state. In contrast, \([I^0:e^−]_{(aq)}\) can be probed by any polarization. The contact pair can dissociate to form \(e^−\) that can be probed by any polarization or recombine to yield \(I^−\) (dashed arrow).
distribution of the CTTS along the surface plane rather than directly into the bulk. Unfortunately, no statistical analysis of the initial localization of the CTTS state relative to the dividing surface was given in the work of Bradforth and Jungwirth.\textsuperscript{25} However, the preferential alignment along the surface plane is consistent with their conclusion that the initial CTTS occupies transient cavities in the first solvation shell around Π, formed by thermal fluctuations. At the interface, there is a water density gradient normal to the surface. According to simulations of the concentration profile at the surface, Π predominantly resides within the region, where the water density falls off toward the vapor phase.\textsuperscript{15} Hence, the occurrence of preformed cavities is expected to be largest in the plane of the surface next to Π rather than directly toward the bulk, where the density is higher. This may also account for the slightly faster rates for solvation observed in the present work compared with the bulk. The CTTS state is not expected to extend significantly into the vapor phase as it is bound for a large part by the polarization of the water around it.\textsuperscript{27} Because there is a double-layer structure at the electrolyte/air interface\textsuperscript{15} that causes a symmetry breaking over ~10 Å, the SHG response may, in principle, arise from this entire region. However, the CTTS state of Π in this second layer is effectively as it is in the bulk and is not expected to show the observed asymmetry. Hence, the asymmetric CTTS dynamics probed here reflect the outermost molecular layers of the water/air interface.

The apparent sub-100 fs phase change observed for the 800 nm PS polarization combination is limited by the time resolution of the experiment, and we can only speculate on its origin. We note that the kinetics show the weakest relative peak at early times, implying a lower sensitivity to the nonequilibrated [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−}. We suggest that perhaps the P output polarization (PS and PP) is not completely insensitive to the CTTS state dynamics but is masked by the much larger signals arising from [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−}. This is not unreasonable because although on average our results show that the CTTS lies mostly along the surface, there will be a distribution such that some component of the transition moment coupling the CTTS state to the Π\textsubscript{(aq)} ground state will lie perpendicular to the surface (as implied in Figure 4b). The 800 nm PS polarization combination then shows evidence of the CTTS state because of its apparent reduced sensitivity to the nonequilibrated [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−}, at the early times.

Given our results, deeper insight into surface solvation of the CTTS state and the [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−} may be attained through theoretical modeling of the expected SHG response. However, this presents a major challenge for theoreticians because of the difficulty in predicting SHG spectra as an infinite sum over all possible pathways involving two states and because of the diffuse nature of the orbitals involved, which include highly polarizable diffuse excited states and the conduction band of water at the interface.\textsuperscript{25}

Finally, we have also probed the kinetics of the [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)} contact pair after it has equilibrated (Figure 3). The amplitude shows a slow decay following the initial CTTS and subsequent solvation dynamics. The model proposed by Stab and Borgis\textsuperscript{25} has frequently been used to account for the kinetics of the equilibrated [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−} which (ignoring the formation of [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−}) involves a competition between geminate recombination to form Π and the dissociation to form I\textsuperscript{0} and e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} (see Figure 4b). Transient absorption\textsuperscript{30,31} and photoelectron spectroscopy\textsuperscript{12} have been used to monitor these kinetics. Although the photoabsorption wavelength and electron binding energy are insensitive to the difference of these two chemical species, analysis of the kinetics enabled Kloepfer et al.\textsuperscript{31} to obtain lifetimes of 33 ps for geminate recombination and 70 ps for dissociation of the contact pair. The SHG signal may be expected to be similarly sensitive to both [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−} and e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} as the absorption spectrum of an interfacial electron has been predicted to be very similar to that of e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} in the bulk.\textsuperscript{25} Therefore, performing the same kinetic analysis of the data in Figure 3 should be appropriate and yields lifetimes of 23 ± 4 and 54 ± 13 ps for geminate recombination and dissociation, respectively. This suggests that the kinetics may be slightly faster at the interface. More striking is the small phase shift associated with the kinetics, which occurs over the first ~30 ps. The phase change indicates that, at the surface, [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−} and e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} can be distinguished. Because the probe wavelength in this experiment was 1320 nm and only the SHG is resonant with transitions of [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−} and e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} (see Figure 4a), the observed phase shift points to a difference in the absorption spectra of [I\textsuperscript{0}:e\textsuperscript{−}]\textsubscript{(aq)}\textsuperscript{−} and e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} (~660 nm) at the ambient water/air interface. This is in contrast with the bulk, where no difference has been noted. The origin for the increased rates of both recombination and dissociation may again be correlated to the lower water density at the interface where the electron resides.

Whether surface electron hydration dynamics are distinct from the bulk has been very topical because of the observation of surface binding of hydrated electrons in water clusters\textsuperscript{33–35} and thin ice films on metal surfaces\textsuperscript{36,37} or metal oxide surfaces.\textsuperscript{38} These surface-bound states are distinct from bulk e\textsuperscript{−}\textsubscript{(aq)} because most of the electron’s distribution is in the vapor phase. The surface-bound state has been observed in a single photoelectron spectroscopy experiment\textsuperscript{9} on liquid water microjets but has not been reproduced in any other experiment. Our experiment shows that, while the initial surface solvation is different, the electron eventually solvates at the interface with physical properties that are very similar to bulk e\textsuperscript{−}\textsubscript{(aq)}. Hence, this would point to a situation in which the electron does not significantly protrude into the vapor phase. This is consistent with the simulations from Uhlig et al. of e\textsuperscript{−}\textsubscript{(aq)} at the water/air interface that indicate that the electron solvates in the interfacial water layer and only ~10% of the electron distribution extends into the vapor phase.\textsuperscript{39} Nevertheless, the proximity to the vapor phase may have important consequences on its chemical properties, as recently implicated in plasma chemistry at the water/air interface.\textsuperscript{40} A very recent sum-frequency generation study has also shown a distinctive vibrational spectrum for water interacting with the surface e\textsuperscript{−}\textsubscript{(aq)}\textsuperscript{−} which resembles the vibrational spectrum of an excess electron in water clusters but not e\textsuperscript{−}\textsubscript{(aq)} in the bulk, suggesting the binding site at the interface may be more distinctive than previously thought. These sum-frequency generation experiments are only comparable to the present experiments after ~50 ps, where e\textsuperscript{−}\textsubscript{(aq)} remains at the surface, but may reflect our suggestion that the e\textsuperscript{−}\textsubscript{(aq)} is solvated within a reduced density water environment at the interface, where the hydrogen-bonding network differs to bulk water and may be more closely related to water clusters.

### EXPERIMENTAL METHODS

The time-resolved phase-sensitive lock-in SHG experiment used here has been described in detail elsewhere.\textsuperscript{23} The pump beam was derived from an optical parametric amplifier (OPA) pumped by an amplified Ti:sapphire laser system and yielded pulses of 250 nm and ~2.5 μJ pulse\textsuperscript{−1} that were focused at the
interface of an aqueous 2 M NaI solution. The probe beam was derived from either the same OPA (1320 nm) or the fundamental of the Ti:sapphire amplifier (800 nm), and these were focused onto the same spot on the surface with an angle of incidence of 70° for the probe and 67° for the pump. The pump and probe laser shared the same plane of incidence. The probe produced SHG, a part of which reflected from the surface. Additionally, a fraction of the probe also reflected from the sample surface and propagated collinearly with its SHG. Both the SHG and reflected probe light were then refocused onto a reference surface ([110]-GaAs), where the probe produced a second SHG field that acted as a local oscillator (LO). The LO interfered with the sample SHG that was reflected from the reference surface. The desired polarization was selected using a Glan-Taylor polarizer, and the probe fundamental was removed using a prism and filters. The SHG photons were detected using a photomultiplier tube. The phase of the interference between the LO and was controlled by mounting the reference surface on a translation stage: The different phase velocities of the probe fundamental and its SHG in air allowed the phase between the two sources of SHG to be varied by changing the distance between the sample and reference surfaces. To remove the large constant signal primarily from the LO, we employed a lock-in measurement. In every second laser-shot, a 2 mm SF10 or fused silica window was introduced in the beam path between surface and reference surfaces. To remove the large constant signal primarily from the LO, we employed a lock-in measurement. Drifts in signal due to changes in surface level of the solution were accounted for in air allowed the phase between the two sources of SHG to be changed the distance between the sample and reference surfaces. The temporal resolution of the experiment was ~100 fs.

The pump wavelength was chosen to be on the long-wavelength side of the lowest energy bulk $\Gamma$ CTTS transition because previous SHG and photoelectron spectroscopy studies suggested that the transition is red-shifted for $\Gamma$ at the surface compared with the bulk. We performed experiments using both the S and P polarizations for the pump, but these showed no differences in the results. All of the results presented were taken with an S-polarized pump beam. Drifts in signal due to changes in surface level of the solution were accounted for by performing periodic background measurements in which the pump was blocked. Over a kinetic scan, these background measurements were fitted to a straight line, and this was subtracted from the pump–probe signal. Hence, the kinetic measurements only represent the pump–probe signal arising from the pump (or other products), and the constant background from the electrolyte solution is removed. For some polarizations (primarily PS, but also PP) there is also a “pump–probe signal” that persists between laser pulses due to long-lived products. This was also removed and is discussed in the supporting materials.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01985.

S.1. Global fitting of amplitude and phase. S.2. Estimate of relative signal levels. Table S1: Comparison between the relative pump–probe signal strengths at different polarizations and wavelengths. S.3. Consideration of other sources of SHG. S.4. Long-lived products. Figure S1: Unsubtracted PS polarization data recorded at 1320 nm, with the subtracted data shown in Figure S2. S.5. Timescale fitting. Figure S2: Fits of amplitude for PP, PS, and SMix polarization. Figure S3: Fits of phase for SMix at 1320 nm fundamental. (PDF)

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**Notes**

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