Ultrafast Dynamics of Water Radiolysis: Hydrated Electron Formation, Solvation, Recombination, and Scavenging

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A schematic diagram of our experimental apparatus is shown in Figure S1 in the Supporting Information. A liquid microjet of 50–60 mmol/L NaCl aqueous solution was discharged into a photoinization chamber from a 25 μm inner-diameter fused silica capillary at a flow rate of 0.5 mL/min. NaCl was dissolved to suppress electrokinetic charging of the microjet.

The photoionization chamber was evacuated by a turbomolecular pump (1400 L/s) and an additional liquid-nitrogen-cooled trap to achieve a pressure of 10^{-6} Torr during the measurements. The photoelectron kinetic energy distribution was measured using a magnetic bottle time-of-flight spectrometer with a 1.3 m long flight path and a SmCo permanent magnet and a solenoid coil (300 turns/m, 3.0 A). The permanent magnet created a magnetic field of 300 mT at the ionization point, and the solenoid created a magnetic field of 1 mT along the spectrometer. The pressure in the spectrometer was <3 × 10^{-7} Torr. Laser pulses irradiated the liquid jet 1 mm downstream from the nozzle. The energy resolution of the electron spectrometer was 50 meV. We applied a bias voltage of +0.8 V to the spectrometer to increase the kinetic energy of electrons to ensure a uniform transmission efficiency through the spectrometer independent of the initial kinetic energy. The liquid nozzle was temperature-controlled at 18 °C. We employed four different excitation schemes involving 160 nm one-photon, 133 nm one-photon, 267 nm two-photon, and 226 nm two-photon absorption. The probe wavelength was 267 nm in all cases. The pump-and-probe pulses were prepared as follows. The output of a Ti:sapphire regenerative amplifier (800 nm, 1 kHz, 35 fs) was split into three beams with pulse energies of 1.7, 0.7, and 1.8
The electronically excited state (11B1) due to electron promotion eV, respectively. The former corresponds to the two-photon ionization of NO. The cross-correlation between the 226 nm pump and the 267 nm pump pulses was measured using the (1 + 1′) nonresonant two-photon ionization of Xe to be 70 fs (fwhm) for the 160 nm pump pulses and 80 fs for the 133 nm pump pulses. The cross-correlation between the 226 nm pump and the 267 nm probe pulses was measured to be 170 fs using (1 + 1′) resonant two-photon ionization of NO.

Figure 1a shows the absorption spectrum of water vapor. The first and second UV absorption bands occur at 7.4 and 9.6 eV, respectively. The former corresponds to the first electronically excited state (1B1*) due to electron promotion from the highest occupied molecular orbital (HOMO; 1b1) to the antibonding/Rydberg 4a1 molecular orbital. The second electronic state is 2A1 and is associated with electron promotion from the HOMO (1b1) to the 3p Rydberg orbital in the Franck-Condon region, but the nuclear motion changes the electronic character to 4a1,σ∗ ← HOMO − 1 (3a1). Water molecules excited to the 1B1 and 2A1 states undergo ultrafast OH bond rupture.18,19 Figure 1b,c, respectively, shows the one-photon and two-photon absorption spectra of liquid water. The 1B1 absorption band for liquid water is blue-shifted from that for water vapor by 0.9 eV due to hydrogen bonding and Pauli repulsion of electron clouds in the condensed phase.20,21,22 The nature of the excited electronic states for liquid water is generally more complex than that for isolated water molecules. For example, the Rydberg states in the gas phase are similar to Wannier excitons in solid-state physics, and they are shifted and energetically broadened in liquid water. The polarization-dependent two-photon absorption spectrum of liquid water reported by Elles et al. suggested the occurrence of electronic transitions to different excited states, namely, 1B1 and 2A1, respectively, at 8.3 and 9.8 eV, and 3p Rydberg states at 9.2, 9.8, and 10.2 eV, as indicated in Figure 1d.23 Theoretical studies indicate that the 1B1 state in liquid water is predominantly a localized excited state involving electron promotion from 1b1 to 4a1,σ* in a single molecule.24,25,26 (We use the symmetry notation in the C2v point group for liquid water throughout this Letter.) The states above 9 eV will have a larger spatial extension of the electronic wave function. In the present study, we employ one-photon excitation at 7.7 and 9.3 eV and two-photon excitation at 9.3 and 11.0 eV.

Figure 2 shows the time-resolved photoelectron spectra measured for the three excitation energies of (a) 7.7, (b) 9.3, and (c) 11.0 eV. The spectra are plotted against the electron binding energy (eBE), given by the difference between the probe photon energy (4.6 eV) and the measured electron kinetic energy. One-color background signals created by the pump-and-probe laser pulses have already been subtracted. The pump-and-probe pulse intensities were adjusted to induce comparable one-color background photoemission signals. The intensity ratio between the two-color and one-color signals was 4:1 and 1:1 for the excitation at 160 and 133 nm, respectively, whereas the ratio for 226 nm two-photon excitation was only 0.3:1 at the delay time of 200 fs. The distributions were corrected using the spectral retrieval method27 (see the Supporting Information for more details) for the influence of inelastic scattering of electrons in liquid water. The vertical eBE (VBE), which corresponds to the peak position in the eBE spectrum of water vapor reproduced from ref 26. (b) One-photon and (c) two-photon absorption spectra of liquid water reproduced from refs 20 and 23, respectively. The arrows indicate excitation energies of 7.7, 9.3, and 11.0 eV. The wavelength for one-photon absorption is also indicated. (d) Decomposition of two-photon absorption spectra into five components, as proposed by Elles et al.23
The time evolution of eBE can be characterized using a time correlation function defined as follows:

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\langle \text{eBE}(t) \rangle = \frac{\langle \text{eBE}(t) \rangle - \langle \text{eBE}(\infty) \rangle}{\langle \text{eBE}(0) \rangle - \langle \text{eBE}(\infty) \rangle}
\]  

(1)

where \(\langle \text{eBE}(t) \rangle\) is the averaged eBE value at time \(t\). We found that \(c(t)\) is well expressed using a biexponential function at all three excitation energies studied in the present work, and the time constants were 0.2 and 1.0 ps (7.7 eV), 0.3 and 0.9 ps (9.3 eV), and 0.2 and 2.0 ps (11 eV). These time constants are in good agreement with the known solvation times for liquid water\(^{27-30}\) and TAS results.\(^{10,12,31-33}\) For example, the solvation times for \(e_{\text{aq}}^-\) in the ground state after internal conversion from the first excited state were previously determined by TRPES to be 0.2 and 1.0 ps.\(^{28,30}\) A TAS study by Vilchiz et al. also gave an estimated solvation time of 0.35 ps for 9.3 eV excitation of liquid water.\(^{12}\) The solvation times are predominantly determined by solvent responses, and they only weakly depend on the generation process for \(e_{\text{aq}}^-\).

Depopulation of \(e_{\text{aq}}^-\) occurs owing to geminate recombination with OH or \(H_2O^{+}\)\(^{35,36}\), of which recombination with OH is more important.\(^{5,15}\) Figure 3a shows the decay profiles for the photoelectron intensity normalized at 0.2 ps. The population decay curves can be expressed using a triexponential function with the time constants listed in Table S2, the depopulation time increases for higher excitation energy. The solvent isotope effect was also examined for 9.3 eV one-photon excitation, and the time constants for D\(_2\)O were found to be slightly greater by a factor of 1.2 to 1.4, similar to the case of diffusive geminate recombination in a charge-transfer-to-solvent (CTTS) reaction from I\(^-\) to liquid water.\(^{37}\) The signal intensity for the longest delay time of 100 ps in Figure 2 gives an electron survival probability \(\Omega(t = \infty)\) of 0.06 (7.7 eV), 0.26 (9.3 eV), and 0.67 (11 eV), indicating that higher excitation energy enables an electron to move further away from the recombination partner. It should be noted that these values are systematically smaller than the previous estimates by TAS,\(^{35,36}\) for example, 0.36 (8.3 eV) and 0.50 (9.3 eV).\(^{14}\) Because the photoabsorption wavelength for \(e_{\text{aq}}^-\) rapidly shifts from the infrared to the visible region owing to the ultrafast solvation/thermalization dynamics in liquid water,\(^{11}\) TAS generally starts monitoring the population of \(e_{\text{aq}}^-\) 3–5 ps after their generation, and the initial dynamics are often missed. The diffusive recombination dynamics after 3 ps is reasonably well described using the independent reaction time (IRT) model proposed by Pimblott,\(^{36}\) and the depopulation within 3 ps is also assumed to obey this model implicitly. However, some TAS studies examined subpicosecond spectral evolution to elucidate the thermalization and depopulation of excess

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**Figure 2.** Photoelectron spectra measured with several excitation schemes. Photoelectron spectra measured with (a) 160 nm pump and 267 nm probe, (b) 133 nm pump and 267 nm probe, and (c) 226 nm two-photon pump and 267 nm probe. The horizontal axis is the pump–probe delay time on a linear scale up to 5 ps and a logarithmic scale after that. The vertical axis is the eBE. (d–f) VBE extracted from the data in panels a–c, respectively. Coherent artifacts have been removed using global fitting for panels d–f. VBE curves are reported in ref.\(^{34}\) for water clusters using one-photon absorption at 133 and 80 nm are, respectively, shown in panels e and f for comparison.

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**Figure 3.** Depopulation of \(e_{\text{aq}}^-\). (a) Depopulation time profile for \(e_{\text{aq}}^-\). The horizontal axis is linear up to 5 ps and logarithmic after that. The photoelectron signal intensity is normalized at 0.2 ps. The typical standard deviation for the 11.0 eV data is shown as an error bar at 3 ps. The lines are the best least-squares fits using a triexponential function. (b) Survival probability. Filled color circles indicate the present work, gray squares indicate the results from ref.\(^{14}\), and gray triangles indicate the results from ref.\(^{7}\), based on TAS. The survival probability corrected for geminate recombination within 5 ps is shown in black. The correction factors for photon energies other than 7.7, 9.3, and 11 eV were linearly interpolated from those at 7.7, 9.3, and 11 eV.
electron transfers. Hertwig et al. suggested that a significant fraction of $e_{aq}$ is lost long before the system is thermalized, and Vilchez et al. argued that 20% of the population decays with a time constant of 1.5 ps for the two-photon excitation of liquid water at 255 nm. As seen in Figure 3a, our TRPES results unambiguously show the occurrence of the ultrafast depopulation of $e_{aq}$ within a picosecond, and the intensity drops to 22 (7.7 eV), 45 (9.3 eV), and 70% (11 eV) in the first 5 ps. Thus the discrepancy between TRPES and TAS is primarily attributed to an underestimation of the ultrafast depopulation within the first 5 ps by TAS. We estimated the reduction factor due to depopulation in the first 5 ps for various excitation energies by interpolating the values measured at 7.7, 9.3, and 11 eV. When we multiply these factors and the survival probabilities previously reported by TAS, we find reasonable agreement with our $\Omega(t = \infty)$ values, as shown in Figure 3b.

For a more detailed comparison with the previous TAS studies, we analyzed our TRPES data using the IRT model for delay times greater than 5 ps. This is described in detail in the Supporting Information. TRPES data obtained using two-photon excitation are in excellent agreement with TAS results using the two-photon scheme. On the contrary, one-photon excitation yielded smaller electron survival probabilities and smaller electron ejection lengths than two-photon excitation for the same excitation energy. This may suggest that the two-photon excitation experiment induces, in part, higher multiphoton effects, resulting in a slightly larger ejection length. An alternative explanation is that one-photon and two-photon excitation create multiple electronic states, such as valence and Rydberg, with different ratios, which lead to slightly different dynamics for electron ejection and geminate recombination.

Recently, Svoboda et al. performed TRPES experiments on water clusters with an approximate aggregation number of 400. At an excitation energy of 9.3 eV, they observed that the VBE appears at 2.5 and then progressively increases to 3.7 eV (Table S2) determined for clusters are considerably shorter than the values of 1.04 and 20 ps for bulk water, as shown in Figure 2e. On the contrary, the depopulation time constants of 0.44 and 8.0 ps that they determined for $e_{aq}$ in $(H_2O)_{400}$ clusters are considerably shorter than the values of 1.04 and 20 ps (Table S2) determined for $e_{aq}$ in bulk water in the present work. The significant difference in geminate recombination dynamics between the cluster and bulk is presumably attributed to the small dimensions of the former. The electron ejection length upon 9.3 eV excitation of liquid water is estimated to be 0.7 to 1.0 nm (Table S5), which is comparable to or even greater than the geometrical size of $(H_2O)_{400}$ clusters. Thus the initial separation between $e_{aq}$ and its recombination partner is smaller in a cluster than in bulk liquid, leading to faster recombination with OH (and H$_3$O$^+$)

The formation of $e_{aq}$ upon UV photoexcitation of liquid water is ascribed to either (i) hydrogen atom transfer or (ii) electron-coupled proton transfer (ECPT) as follows

$$H_2O(aq) + hv \rightarrow HO(aq) + H(aq)$$  

$$H(aq) + H_2O(aq) \rightarrow H_2O(aq)$$  

$$H_2O(aq) \rightarrow H_3O^+(aq) + e_{aq}$$  

or

$$2H_2O(aq) + hv \rightarrow H_3O^+(aq) + OH(aq) + e_{aq}$$  

where $H_2O$ in eqs 3 and 4 is known as a “Rydberg radical”, in which an electron is weakly bound to H$_3$O$^+$, so that the CTTS reaction is expected to occur from H$_2$O to liquid water to produce H$_3$O$^+$ and $e_{aq}$. The 1$^1B_1$ electronic state produced by 7.7 eV excitation has a similar electronic character to that in the gas phase, so that it is expected to undergo ultrafast OH bond rupture within several femtoseconds. Thus our experimental results imply that the H atom transfer process creates $c_{aq}$. Previously, Thomsen et al. studied 9.3 eV photolysis of liquid water using two-photon excitation and TAS and concluded that the OH population estimated using UV absorption is greater than the population of $e_{aq}$ suggesting that H atom transfer contributes to $c_{aq}$ formation, at least to some extent, at this energy. In view of the increased survival probability at a higher excitation energy and the delocalization of the calculated electronic wave functions above 9 eV, it is likely that different $c_{aq}$ formation channels, such as ECPT, become operative.

In addition to OH and H$_3$O$^+$ created upon charge separation in liquid water, scavengers that capture excess electrons can be added to an aqueous solution. The effectiveness of each scavenger has been characterized by pulse radiolysis using the parameter C$_{17}$, which is defined as the scavenger concentration required to reduce the initial $c_{aq}$ concentration to 37% of the value for pure water. The “initial” in this definition is the shortest experimental time resolution of 10–30 ps in conventional pulse radiolysis. The C$_{17}$ value is 1.6 mol/L for NO$_3^-$ and 0.42 mol/L for NO$_2^-$, indicating that NO$_3^-$ is a stronger scavenger. Clearly, the elucidation of the scavenging dynamics requires a high experimental time resolution. The scavenging can be divided into static scavenging, which occurs instantaneously without diffusion, and diffusion-controlled dynamic scavenging, and these should be clearly differentiated. Kee et al. performed two-photon excitation of liquid water at 266 nm (9.3 eV) and TAS at 650 nm to study electron scavenging; unfortunately, however, the dynamics within a femtosecond time scale could not be followed with TAS for ultrafast spectral shifts of $c_{aq}$. In the present study, we explored electron scavenging by NO$_3^-$ in the femtosecond to picosecond time range using TRPES. We performed the scavenging experiments with one-photon excitation at 160 and 133 nm but did not perform them with two-photon absorption at 226 nm because NO$_3^-$ has strong photoabsorption around 200 nm. Photoabsorption by NO$_3^-$ at 160 nm is negligible in comparison with that by liquid water. NO$_3^-$ can be directly ionized at 133 nm; however, even if we assume the photoabsorption cross-section of NO$_3^-$ at 133 nm to be as large as 50 Mb, the ionization probability is calculated to be only $10^{-4}$ owing to a very small photon flux ($2 \times 10^{15}$ photons s$^{-1}$ cm$^{-2}$). The excess electrons generated by this process are only 7% with respect to the photoionization of NO$_3^-$ those in Figure 3a, and they indicate only geminate recombination with OH and H$_3$O$^+$.

Figure 4 shows the time profiles for total photoelectron intensity measured for various NO$_3^-$ concentrations. The time evolution of $eBE$ was identical to that in pure water and is not shown here. The decay curves for [NO$_3^-$] = 0 are the same as those in Figure 3a, and they indicate only geminate recombination with OH and H$_3$O$^+$. The addition of NO$_3^-$ introduces two effects: a reduction of the initial population of $c_{aq}$ and an acceleration of the decay on a picosecond time scale (Tables S7 and S8). Static scavenging already occurs within our time resolution of 70–80 fs; the initial $c_{aq}$ population

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From the precisely determined. Static and dynamic scavenging of clearly identi
rapid eBE shift due to solvation in liquid water. Ultrafast
is in reasonable agreement with the value of 0.42 mol/L

![Image](https://pubs.acs.org/10.1021/acs.jpcl.0c01468)

**Figure 4.** Scavenging effect observed in the 7.7 and 9.3 eV experiments. Total photoelectron intensity as a function of delay time for (a) 7.7 and (b) 9.3 eV excitation at different NO₃⁻ concentrations. The shaded area shows the standard deviation of the intensity. The solid lines are best fits using a biexponential function. The sub-picosecond time constant decreased with increasing concentration of NO₃⁻ from 0.75 to 0.5S in 7.7-eV experiment and from 1.04 to 0.33 in 9.3-eV experiment. See Table S8 for details.

diminished by 11% at [NO₃⁻] = 0.1 mol/L for 9.3 eV excitation. Our experimental results strongly suggest that static scavenging is caused by quenching of the photoexcited electronic states of liquid water by NO₃⁻. They also confirm the conjecture based on Monte Carlo track structure simulations that NO₃⁻ at a high concentration quenches the excited states of liquid water and inhibits H₂ formation in liquid water radiolysis. Figure 4 also shows that the static scavenging efficiency is greater for 9.3 than 7.7 eV at the same [NO₃⁻], which indicates that scavenging depends on the nature of the excited electronic states of liquid water created by photoexcitation. Initial dynamic scavenging occurs quite rapidly, possibly with an elevated local temperature, and observation of the femtosecond dynamics is required to differentiate the static and dynamic scavenging yields correctly. From the c₇7 population at 5 ps for various [NO₃⁻], C₇7 is estimated to be 0.94 and 0.46 mol/L for excitation energies of 7.7 and 9.3 eV, respectively. The estimated C₇7 value for 9.3 eV is in reasonable agreement with the value of 0.42 mol/L previously reported using pulse radiolysis. In conclusion, we investigated the c₇7 formation induced by the UV excitation (7.7–11.0 eV) of liquid water using ultrafast photoelectron spectroscopy of a liquid microjet. A vacuum UV laser with photon energies of 7.7 and 9.3 eV was employed for one-photon excitation to the 1B₁ and 2A₁ states, whereas two-photon excitation was also performed at 9.3 and 11.0 eV for comparison. The photoelectron spectra of c₇7 exhibited a rapid eBE shift due to solvation in liquid water. Ultrafast geminate recombination on a subpicosecond time scale was clearly identified, and the electron survival probability was precisely determined. Static and dynamic scavenging of c₇7 with NO₃⁻ was investigated on a femtosecond time scale, and we obtained evidence that the excited electronic states are rapidly quenched by NO₃⁻ in competition with ultrafast OH bond rupture. The c₇7 formation at 7.7 eV is ascribed to the H-atom-transfer process, but it is plausible that additional c₇7 formation channels open at higher energies.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.0c01468.

Details of experimental apparatus, spectral retrieval method and sensitivity to the choice of basis function, fitting of decay profiles for photoelectron intensity using the tri-exponential function, comparison of 266 nm two-photon excitation and one-photon, independent reaction time model analysis, and results of scavenging experiment Figure S1. Schematic diagram of the optical setup for VUV photoelectron spectroscopy. Figure S2. eBE distributions for hydrated electrons obtained using different methods. Figure S3. Comparison of retrieved photoelectron spectra calculated from an identical data set obtained using 133 nm pump and 267 nm probe pulses. Figure S4. Snapshots of the retrieved spectra shown in Figure S3. Figure S5. Comparison of photoelectron spectra for 133 nm one-photon and 267 nm two-photon excitation. Table S1. Comparison of time constants obtained for c(t) calculated from (eBE) and VBE after spectral retrieval using G(E) and G(E). Table S2. Comparison of time constants for depopulation. Table S3. Time constants obtained by global fitting. Table S4. Parameters for IRT analysis. Table S5. Comparison of electron ejection length (rₑ). Table S6. Comparison of electron survival probability Ω. Table S7 Photoelectron intensities as function of delay time and [NO₃⁻]. Table S8. Decay time constants as a function of [NO₃⁻] (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### REFERENCES


