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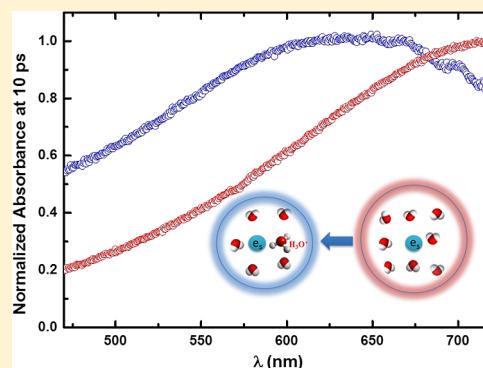
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## S Supporting Information

**ABSTRACT:** The reaction between the solvated electron and hydronium cation  $\text{H}_3\text{O}^+$  in water constitutes a fundamental reaction in chemistry. Due to significant rearrangement of solvent molecules around both the electron and  $\text{H}_3\text{O}^+$ , the reaction rate of this process is not controlled by diffusion. The presence of a reaction barrier suggests the formation of an intermediate that has so far not been observed. Here, the time-resolved visible absorption spectra in three concentrated acid solutions, perchloric, sulfuric, and phosphoric, at various concentrations are recorded by the picosecond pulse radiolysis method. In contrast to previous reports, a strong blue shift of the absorption band of the solvated electron in acidic solutions compared to neat water is clearly observed, consistent with formation of a pair between the solvated electron and hydronium cation.

## SECTION: Kinetics and Dynamics

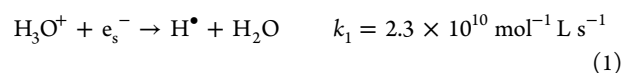


The solvated electron is a key intermediate in radiolysis- and photolysis-induced processes in liquids. Observed for the first time in 1962, the hydrated electron has been the subject of extensive works by several methods such as pulse radiolysis and laser photolysis.<sup>1</sup> Its absorption spectrum displays a broad, structureless band with a maximum at around 715 nm in neat water attributed to the transition from the ground s-like state to p-like states. During the last 50 years, the reactivity of the hydrated electron with different solutes has been widely studied.<sup>2–5</sup> Four types of solutes can be distinguished with regard to their reactions with solvated electrons, (i) scavengers with a rate constant controlled by diffusion, (ii) solutes reacting with a solvated electron but with a rate constant lower than that controlled by diffusion, (iii) solutes not reacting with a solvated electron but forming a pair with it, and (iv) solutes not interacting with a solvated electron. Here, the second and third cases attract our attention.

In aqueous solutions, alkaline and earth alkaline metal ions and f-block trivalent cations such as  $\text{Tb}^{3+}$  form ion pairs with a hydrated electron. These pairs,  $(\text{M}^{x+}, \text{e}_s^-)_{\text{water}}$  are stable even on the microsecond range. The absorption maximum of the hydrated electron/metal cation pair shifts from 715 nm in neat water to shorter wavelengths while keeping the same shape of the absorption band.<sup>6</sup> The origin of the spectral blue shift of these pairs has been attributed to a contraction of the radius of the solvated electron cavity. It has been shown that the blue shift increases continuously with the salt concentration without any change in the absorption band shape.<sup>7</sup> It was also reported that the spectral shift depends on the characteristics of the solution such as cation size and charge (through charge densities) or dissociation degree of the salt (partial screening of the cation charge for incomplete dissociation).<sup>8</sup> In the case of a

sodium cation, molecular dynamics simulations suggested a possible formation of a contact cation/electron pair. The simulation of the pair also showed a blue shift of about 0.3 eV, attributed to a stronger stabilization of the s-like state than the p-like state in the close presence of the cation.<sup>9</sup>

In some cases, the reaction of the solvated electron with the solute is effective, but it is not diffusion-controlled. Due to significant solvent rearrangement, an activation barrier slows down the reduction reaction. Therefore, it could be possible to observe the pair formed between the solute and solvated electron before the effective reduction reaction. One of the most fundamental reactions of the solvated electron is the reaction with hydronium cation  $\text{H}_3\text{O}^+$ . The hydronium cation is always present in water, and it is also used to scavenge a solvated electron to form a hydrogen atom in acidic solutions. It is known that this reaction is not diffusion-controlled and presents an activation energy of 0.15 eV.<sup>3,10</sup>



The value of the rate constant is at least 3–5 times lower than that expected for the diffusion-controlled rate constant.<sup>11</sup> Picosecond pulse radiolysis showed that the rate constant of reaction 1 in concentrated acid solution ( $1.2 \times 10^{10} \text{ mol}^{-1} \text{ L s}^{-1}$ ) is somewhat smaller than that obtained from microsecond pulse radiolysis in dilute solutions due to the change of the solute activity.<sup>12,13</sup> Consequently, the dominant reaction of the

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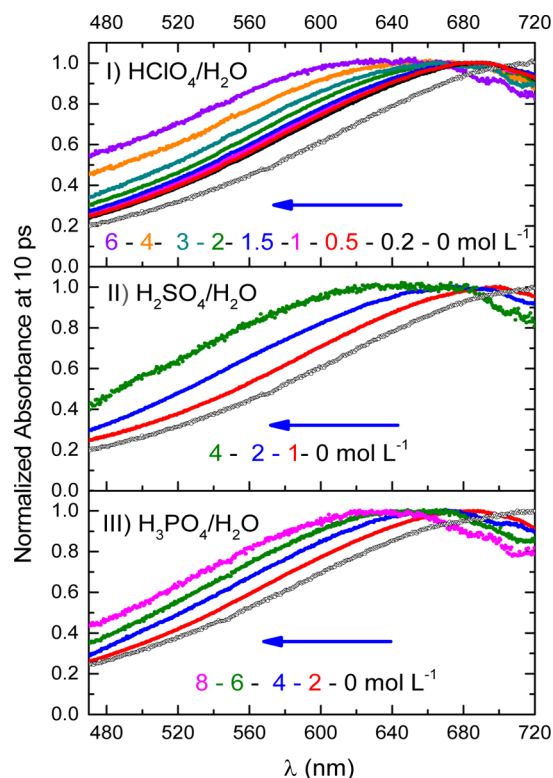
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hydrated electron in radiation-induced spurs is through the faster reaction with the  $\text{OH}^\bullet$  radical. Despite the apparent simplicity of reaction 1, it has been debated by several groups.<sup>14</sup> The Bronsted correlation of solvated electron reaction rates observed for an important number of acids suggested firmly that reaction 1 is a proton-transfer reaction rather than an electron-transfer one. A long-lived  $\text{H}_3\text{O}^\bullet$  radical intermediate in reaction 1 was suggested, but no clear evidence was reported by time-resolved transient absorption down to the picosecond time scale and ESR spectroscopy.<sup>14–16</sup> The reaction between the hydrated electron and  $\text{H}_3\text{O}^+$  was also studied by considering the temperature effect on the overall rate constant to derive the reaction rate constant.<sup>17</sup> A recent *ab initio* simulation suggests that the  $\text{H}_3\text{O}^\bullet$  radical may be present as an intermediate in reaction 1. The radical is stable in the gas phase, but in the presence of a few water molecules, it is separated to a delocalized  $\text{H}_3\text{O}^+\cdots\text{e}^-$  solvent-separated pair.<sup>18</sup> It was also reported that the absorption spectrum of the solvated electron is not affected in acidic solution.<sup>12</sup> Normalized absorption measurements showed that the transient species observed in 0.1 up to 1 mol L<sup>-1</sup>  $\text{HClO}_4$  display the absorption spectra of the solvated electron in neat water with a maximum at around 715 nm. The initial radiolytic yield of solvated electron was found to be also constant for solutions with concentrations of  $\text{H}_3\text{O}^+$  up to 2 mol L<sup>-1</sup>, meaning that the  $\text{H}_3\text{O}^+$  does not react with the precursor of the hydrated electron.<sup>19</sup> Nevertheless, femto-second laser photolysis measurements showed that the initial transient absorption in the strong acidic aqueous solution is lowered (by 10%) compared to that observed in pure water.<sup>20</sup> Kinetics simulation showed that the probability of the reaction between the solvated electron and  $\text{H}_3\text{O}^+$  in the pair is small and that the encounter duration can be on the order of a few picoseconds.<sup>21</sup> It is interesting that a femtosecond photolysis study of an 11 mol L<sup>-1</sup>  $\text{HCl}$  solution showed that a nonsolvated electron could be formed in the solvation shell of  $\text{H}_3\text{O}^+$ , forming a  $(\text{H}_3\text{O}^+, \text{e}^-)_{\text{water}}$  pair displaying an absorption spectrum located at around 900 nm.<sup>22</sup> However, the authors did not observe the pair between the solvated electron and hydronium cation,  $(\text{H}_3\text{O}^+, \text{e}_s^-)_{\text{water}}$ .

In the present work, the influence of  $\text{H}_3\text{O}^+$  on the absorption spectrum of the hydrated electron is studied by picosecond pulse radiolysis in highly concentrated perchloric, sulfuric, and phosphoric acid solutions. The results presented here are in disagreement with previous reports obtained by picosecond pulse radiolysis.<sup>19</sup> The observed spectral shift of the absorption band and the initial yield of the solvated electron are discussed, and it is shown that the solvated electron forms a transient pair with  $\text{H}_3\text{O}^+$ . The characteristic of hydrogen atom formation is compared for both pairs  $(\text{H}_3\text{O}^+, \text{e}^-)_{\text{water}}$  and  $(\text{H}_3\text{O}^+, \text{e}_s^-)_{\text{water}}$ .

The absorption spectra in pure water and in three acid solutions with various concentrations are recorded at 10 ps after the time zero (see Figures 2–4 in the Supporting Information (SI)). It is known that the radicals  $\text{ClO}_4^\bullet$ ,  $\text{SO}_4^\bullet$ , and  $\text{H}_2\text{PO}_4^\bullet$  are formed by the direct radiation effect in perchloric, sulfuric, and phosphoric acid solutions, respectively.<sup>23,24</sup> They absorb in the UV–visible at around 370, 450, and 520 nm, respectively, with small extinction coefficients. Their low contribution is subtracted from the observed absorption band before normalization (Figure 1).

At 10 ps, the electron induced by an electron pulse in solution is already solvated, and the presolvated electron signature is not present in the absorption band. For the three acidic solutions, the blue shift of the absorption band of the



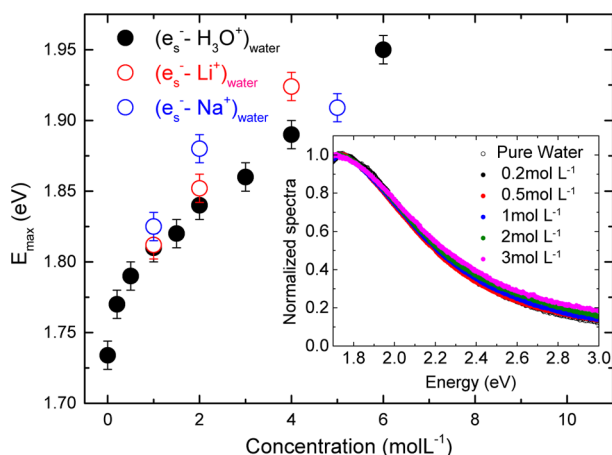
**Figure 1.** Normalized absorption spectra measured at a delay of 10 ps in three acid solutions (perchloric, sulfuric, and phosphoric acids) at different concentrations.

solvated electron is obvious. The shape of the observed spectra does not depend on time; only the intensity decreases with increasing time delay (see Figures 5 and 6 in the SI). The blue shift is most pronounced for perchloric acid. As the dissociation of perchloric acid is greater than that of phosphoric acid, the blue shift for the solution containing 6 mol L<sup>-1</sup>  $\text{HClO}_4$  is larger than for that containing 2 mol L<sup>-1</sup>  $\text{H}_3\text{PO}_4$  (3 equiv of  $\text{H}_3\text{O}^+$ ).<sup>25–27</sup>

Even for 0.2 and 0.5 mol L<sup>-1</sup>  $\text{HClO}_4$  solutions, the shift is observed. The maximum of the absorption band for 0.2 and 0.5 mol L<sup>-1</sup> is located at  $696 \pm 5$  and  $692 \pm 5$  nm, respectively. For the lowest concentrations (0.2 and 0.5 mol L<sup>-1</sup>), the shift of the absorption band of the solvated electron is clearer observed in the visible part of the absorption band. The variation of the maximum of the electronic transition observed in the case of perchloric acid exhibits a shift of 0.22 eV from pure water to 6 mol L<sup>-1</sup>  $\text{H}_3\text{O}^+$  (Figure 2).

The spectra normalized for amplitude and spectral position (to the value of pure water) show that the shape of the absorption band does not change by increasing the concentration of acid (Figure 2 inset). The only change is that the maximum is shifted to higher energy. This behavior is very similar to the one observed when the solvated electron is paired with metal cations.<sup>7,8</sup>

The blue shift of the absorption band toward the cation concentration is similar to those already reported with small cations such as  $\text{Li}^+$  and  $\text{Na}^+$ , with  $\text{ClO}_4^-$  as the counterion. These observations are in favor of the formation of an intermediate not to be identified as the  $\text{H}_3\text{O}^\bullet$  radical as suggested before but a transient solvent-separated electron and hydronium pair  $(\text{H}_3\text{O}^+, \text{e}_s^-)_{\text{water}}$ .

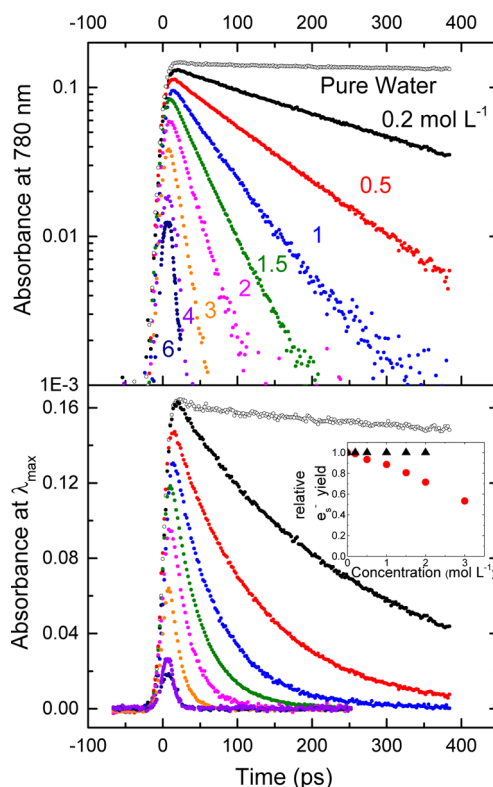


**Figure 2.** Energetic position of the absorption band maximum of the pairs formed by a hydrated electron and  $H_3O^+$  (this work, perchloric acid system),  $Li^+$ , and  $Na^+$ .<sup>8</sup> (Inset) Absorption spectra of the hydrated electron and pair  $(H_3O^+, e_s^-)_{\text{water}}$  formed at different concentrations normalized for amplitude and spectral position. The counterion is  $ClO_4^-$  in all cases.

According to a simple Debye–Smoluchowski model, the rate constant of the pair formation in diluted solution should be around  $10^{11} \text{ mol}^{-1} \text{ L s}^{-1}$ . Therefore, the formation time of the pair is expected to be 50 ps for the lowest concentration solution (0.2 mol L<sup>-1</sup>). However, our measurements do not display any shift of the absorption between 10 and 100 ps. That can be explained by the fact that the solvation dynamics of the electron in highly concentrated acidic solutions is not like the one in neat water. A part of the presolvated electrons could be trapped in the vicinity of  $H_3O^+$ , and consequently, the solvated electrons are formed very quickly in close distance of  $H_3O^+$ . The pairs  $(H_3O^+, e_s^-)_{\text{water}}$  are formed within the apparatus function of our experimental setup. Femtosecond measurements have the potential to reveal the existence of a fully hydrated electron before pair formation.<sup>22</sup>

The blue shift of the absorption band was also observed in low polar solvent such as THF and alcohol when the solvated electron was paired with a metal cation, even at a low concentration of the cation.<sup>28–30</sup> However, it is important to note that water presents a high dielectric constant that is not in favor of pair formation at low concentration of the solutes. That is why our measurements were performed in highly concentrated acid solutions. In highly concentrated solution, the pairing occurs because the distances between the solvated electron and  $H_3O^+$  are very short. For example, in the case of a 6 mol L<sup>-1</sup> solution, this distance is only a few Å, and the solvated electron is in contact distance with  $H_3O^+$ . It should be also noted that the dielectric constant of the highly concentrated solutions is changed compared with that of neat water. In fact, the structure of the solvent is changing by increasing the ionic strength. For example, in phosphoric acid solutions, it is reported that the dielectric constant of the solutions decreases from 78 for neat water to 70, 62, 55, and 44 for 1, 2, 3, and 5 mol L<sup>-1</sup>, respectively.<sup>31</sup> Therefore, a general effect of the ionic strength should be also taken into account for the shift of the absorption band in highly concentrated acidic solutions.

The initial absorbance is decreased by 0, 7, 12, 20, 29, and 47% for the perchloric acid solution at concentrations of 0.2, 0.5, 1, 1.5, 2, and 3 mol L<sup>-1</sup>, respectively (Figure 3 inset). This

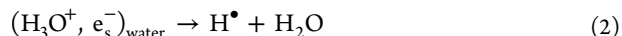


**Figure 3.** Decay of the solvated electron in perchloric acid solution at different concentrations. (Upper part) Logarithmic scale at 780 nm. (Bottom) The absorbance observed at the maximum of the absorption band for each perchloric acid concentration. (Inset) Relative yield of solvated electron deduced from the absorbance at the maximum in this work (red ●) and in ref 19 (▲).

decrease is due to the scavenging of the presolvated electron by  $H_3O^+$ , which was previously considered negligible up to 2 mol L<sup>-1</sup> perchloric acid (Figure 3 inset, black triangles).<sup>19</sup> The reason could be that the shift of the absorption band was not considered. From the analysis, we find the kinetics of  $C_{37}$ , which is defined by a solute concentration that reduces the initial yield of solvated electrons to  $1/e$ , to be around 3.5 mol L<sup>-1</sup>. This value is much larger than that for efficient scavengers of presolvated electrons such as cadmium, selenite, bipyridine, or nitrate. However, it is shown clearly that  $H_3O^+$  scavenges presolvated electrons. The blue shift of the epithermal electron (nonsolvated electron) from  $\lambda > 1300$  to 930 nm observed by femtosecond spectroscopy<sup>22</sup> showed that the  $(H_3O^+, e^-)_{\text{water}}$  has the same spectral trend as  $(H_3O^+, e_s^-)_{\text{water}}$ . However, the lifetime of  $(H_3O^+, e^-)_{\text{water}}$  is very short, and the  $H^\bullet$  atom is formed in less than 1 ps. This ultrafast reaction is in agreement with our observation that the initial yield of solvated electron observed at 10 ps decreases by increasing the concentration of  $H_3O^+$ , showing that the presolvated electron is scavenged partially by  $H_3O^+$ . The formation of the  $H^\bullet$  atom via the ultrashort-lived pair  $(H_3O^+, e^-)_{\text{water}}$  occurs without barrier, and it can be considered as an intraelectron transfer within the pair. Note that the electron in this pair is not solvated. The lifetime of  $(H_3O^+, e_s^-)_{\text{water}}$  is much longer, and first-order kinetics are expected to apply if an intraelectron transfer occurs forming  $H^\bullet$ . As reported above, the reaction rate of the decay is concentration-dependent. In fact, the decays of the pair  $(H_3O^+, e_s^-)_{\text{water}}$  observed in different solutions and at various concentrations are all pseudo-first-order (Figure 3). That



means, contrarily to the case of  $(\text{H}_3\text{O}^+, e^-)_{\text{water}}$ , the channel of the decay of the pair  $(\text{H}_3\text{O}^+, e_s^-)_{\text{water}}$  resulting in a hydrogen atom is not an intraelectron transfer as follow



and this point confirms clearly that the hydrogen atom formation by the solvated electron reaction with  $\text{H}_3\text{O}^+$  is governed by a proton-transfer reaction,<sup>32</sup> which is regulated by a hydrogen network and hopping mechanism of the proton from one water molecule to another one. Therefore, the reaction involves  $\text{H}_3\text{O}^+$  concentration. Consequently, even if the solvated electron is in close contact with  $\text{H}_3\text{O}^+$ , the reaction is not immediate, and as the lifetime of the pair is long enough, even another proton can come into contact and react with solvated electron through the hydrogen network. The difference of energy of the electronic transition between  $(\text{H}_3\text{O}^+, e^-)_{\text{water}}$  and  $(\text{H}_3\text{O}^+, e_s^-)_{\text{water}}$  shows that the first pair is on an energy level raised by 0.35 eV, which is larger than the activation barrier (0.15 eV) for reaction 1. This points out that the reduction reaction giving  $\text{H}^\bullet$  atom could occur via an electron transfer from the presolvated electron, whereas a proton transfer occurs when the electron is fully stabilized by solvation.

The evidence for the formation of a pair between the solvated electron and  $\text{H}_3\text{O}^+$  reported here is an important observation that could lead to a better understanding of structure and reactivity of the solvated electron. In fact, several ab initio computational works have been performed on the ultrafast reaction 1 to describe the essential features of reactive processes of the hydrated electron.<sup>32,33</sup> The observation reported here provides new insight into the discussion concerning the nature of the intermediate and whether reaction 1 is characterized by proton transfer or electron transfer.

## EXPERIMENTAL METHOD

The picosecond pulse radiolysis measurements were performed at the experimental area EA-1 of the ELYSE accelerator facility. The transient absorption electron pulse–optical probe setup is based on the laser–electron intrinsic synchronization resulting from the laser-triggered photocathode detailed elsewhere.<sup>34</sup> The main part of the femtosecond laser output is used to produce the electron pulse that is accelerated to relativistic energies by RF fields and used as the pump. A part of the laser source is split off to generate the optical probe pulse that can be delayed relative to the electron bunch by a mechanical translation stage. As described in ref 35, a supercontinuum generated in  $\text{CaF}_2$  was used as the optical probe and recorded with a multichannel detection system. The electron pump and the broad-band probe beam were directed collinearly through the sample. All of the measurements were made in a fused silica optical flow cell with a 5 mm optical path. Under the experimental conditions, the apparatus function has typically of full width at half-maximum of 12 ps. The measurements were performed at 22.5 °C. The acid solutions were purchased from Sigma-Aldrich. Water for dilution was purified by passage through a Millipore purification system. More details on the setup, the data acquisition, and treatment including the dosimetry are given in the SI (Table 1).

## ASSOCIATED CONTENT

### Supporting Information

Additional experimental details, scheme of the electron pulse–broad-band probe setup and the fused silica optical flow cell, chemical compositions of perchloric acid solutions with different concentrations, absorption spectra recorded at 10 ps after time zero in perchloric acid systems, phosphoric acid systems, and sulfuric acid systems, absorption spectra recorded at different delay times in 0.2 mol L<sup>-1</sup>  $\text{HClO}_4$  aqueous solutions, and normalized absorption spectra recorded at different delay times in 0.2 mol L<sup>-1</sup>  $\text{HClO}_4$  aqueous solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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