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# Reactivity of quasi-free electrons toward $\text{N}_3^-$ and its impact on $\text{H}_2$ formation mechanism in water radiolysis

Denis Dobrovolskii,<sup>a</sup> Sergey A. Denisov,<sup>a</sup> Howard E. Sims<sup>b</sup> and Mehran Mostafavi<sup>\*a</sup>

Picosecond pulse radiolysis measurements were employed to assess the effectiveness of  $\text{N}_3^-$  in scavenging quasi-free electrons in aqueous solutions. The absorption spectra of hydrated electrons were recorded within a 100 ps timeframe across four distinct solutions with  $\text{N}_3^-$  concentrations of 0.5, 1, 2, and 5 M in water. The results revealed a concentration-dependent shift in the maximum absorption spectra of fully solvated electrons. Notably, at 5 M concentration, the maximum absorption occurred at 670 nm, in contrast to 715 nm observed for water. Intriguingly, the formation yield of hydrated electrons within the initial 5 ps electron pulse remained unaffected, showing that, even at a concentration of 5 M,  $\text{N}_3^-$  does not effectively scavenge quasi-free electrons. This is in disagreement with conclusions from stochastic models found in the literature. This observation has an important impact on understanding the mechanism of  $\text{H}_2$  formation in water radiolysis, which we discuss briefly here.

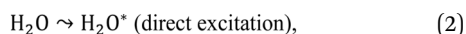
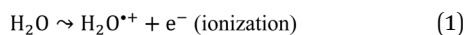
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## Introduction

The radiation chemistry of liquid water is of fundamental importance for various practical applications, particularly in the nuclear power industry, where radiolysis products cause corrosion and  $\text{H}_2$  evolution.<sup>1,2</sup> Still, one century after observations of water radiolysis, the mechanism of radicals and molecular products of water radiolysis in a homogenous step, *ca.* 200 ns after energy deposition in water, are under debate.<sup>3–7</sup> It is generally assumed that when exposed to ionizing radiation, water molecules undergo ionizations and excitations:



After being generated by radiation, the excess electron undergoes a solvation process, quickly becoming fully solvated in water within 1 picosecond, having a broad absorption band, peaking at 715 nm.

The electron can be hydrated in less than 1 ps:



When the dose is low, the hydrated electron remains stable in pure water for up to 1 millisecond. Despite its stability, the solvated electron exhibits high reactivity, participating in various chemical reactions. In diluted aqueous solutions or pure water, where the electron primarily interacts with water molecules, it is denoted by the symbol  $\text{e}_{\text{aq}}^-$ . However, in solutions containing high concentrations of non-reactive metal cations like  $\text{Na}^+$ , which can interact with the electron, the symbol  $\text{e}_s^-$  represents the fully solvated electron.

In one picosecond, these processes result in a cascade of events leading to the formation of free radicals and molecular products along the track of the incident radiation. In pure water radiolysis, they essentially comprise the hydrated electron  $\text{e}_s^-$ ,  $\text{H}^\bullet$ ,  $\bullet\text{OH}$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}_2$ .<sup>2,8,9</sup>

Among these radiolysis products, one of the most interesting is molecular hydrogen,  $\text{H}_2$ , largely due to its mechanism of formation, namely the nature of its precursor(s). Studies of a variety of scavenger systems at high concentrations<sup>4,5</sup> in conjunction with computer simulations<sup>3,10</sup> have suggested that the majority of the total  $\text{H}_2$  yield in  $^{60}\text{Co}$ -radiolysis involves reactions of short-lived, low-energy (“dry” or quasi-free) secondary electrons that have a kinetic energy during the sub-femtosecond physical stage. Four different mechanisms are considered to explain  $\text{H}_2$  production under water radiolysis of which 1–3 occur in less than 1 ps:

(1) The geminate recombination of the quasi-free electron with its short-lived  $\text{H}_2\text{O}^{+\bullet}$  parent cation (or “hole”) due to their Coulomb attraction, which tends to draw them back together:<sup>11–15</sup>

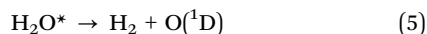
<sup>a</sup> Institut de Chimie Physique, Université Paris-Saclay, CNRS, Bâtiment 349, Orsay, 91405, France. E-mail: [mehran.mostafavi@universite-paris-saclay.fr](mailto:mehran.mostafavi@universite-paris-saclay.fr)

<sup>b</sup> Central Laboratory, National Nuclear Laboratory, Sellafield, Seascale CA20 1PG, UK

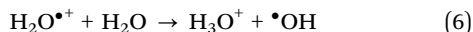




followed by the dissociation of the excited water molecule



where O(<sup>1</sup>D) is the oxygen atom in its singlet state. Note that reaction (4) must take place before the H<sub>2</sub>O<sup>•+</sup> cation whose lifetime is less than a few tens of fs<sup>16,17</sup> undergoes proton transfer to a neighboring water molecule to give the hydronium cation H<sub>3</sub>O<sup>+</sup> and the hydroxyl radical •OH.



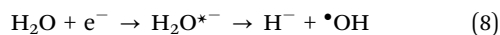
Since reaction (6) is ultrafast, reaction (4) can only involve the quasi-free electrons formed in the vicinity of the parent water cation and occurs in the first steps of their random walk, *i.e.*, in times as short as a few femtoseconds.

(2) Decomposition of H<sub>2</sub>O\* formed by direct excitation<sup>4,11,18–22</sup>

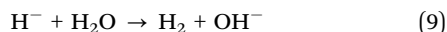
The excited state of water usually undergoes dissociation by forming •OH and •H radicals. However, another channel is considered for the dissociation process by forming H<sub>2</sub> according to the following reaction:



(3) The “dissociative electron attachment” (or DEA) involves the resonant capture of a low-kinetic energy electron by a water molecule:<sup>23–27</sup>

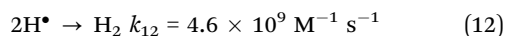
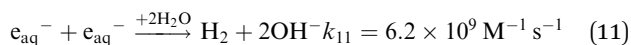
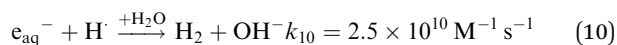


followed by the reaction of the hydride anion with a second water molecule *via* ultrafast proton transfer:



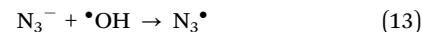
The reactions (8) and (9) are fast and occur in the fs range.

(4) The residual production of H<sub>2</sub> through radiolysis is attributed to three specific radical–radical combination reactions involving the hydrated electron and H• atom.<sup>15,23,28–30</sup> These reactions occur within the expanding tracks *via* diffusion during the nonhomogeneous chemical stage.

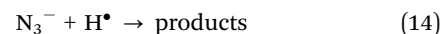


Scavenging methods and simulations are used to evaluate each mechanism's contribution.

Azides, N<sub>3</sub><sup>-</sup>, consisting of three nitrogen atoms arranged linearly, are known for their reactivity and have applications in various fields.<sup>31</sup> The simplest azide is N<sub>3</sub><sup>-</sup> anion, which is very soluble in water.<sup>32</sup> N<sub>3</sub><sup>-</sup> can undergo radiolysis when exposed to ionizing radiation in aqueous solution.<sup>33</sup> It is well-known that azide reacts with OH• radical, forming the azide radical:<sup>34,35</sup>



The radical N<sub>3</sub>• is a less oxidizing species than OH• radical and is used as a one electron oxidizing radical.<sup>36,37</sup> In contrast, the hydrated electron reaction with N<sub>3</sub><sup>-</sup> is very slow, and the value of the rate constant of this reaction is estimated to be lower than 1.5 × 10<sup>6</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>38,39</sup> However, the reaction of N<sub>3</sub><sup>-</sup> with H• atom is fast with a rate constant of *k* = 2.5 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>.<sup>40</sup>



The slow reaction with the hydrated electron and the fast reaction with the H• atom allows N<sub>3</sub><sup>-</sup> as a selective scavenger to deduce information about the mechanism of H<sub>2</sub> formation. Peled *et al.*<sup>39</sup> showed that N<sub>3</sub><sup>-</sup> reduces the yield of H<sub>2</sub>, G(H<sub>2</sub>), from 0.45 × 10<sup>-7</sup> mol J<sup>-1</sup> to 0.157 at 5 M N<sub>3</sub><sup>-</sup> in neutral solutions and from 0.37 mol J<sup>-1</sup> in 0.5 M solution to 0.21 mol J<sup>-1</sup> at 4 M N<sub>3</sub><sup>-</sup> in alkaline solutions. The hydrated electron reacts with azide very slowly, and the presence of 1 M N<sub>3</sub><sup>-</sup> was found not to affect the solvated electron spectrum at 100 ns in their work.

In competition experiments between N<sub>3</sub><sup>-</sup> and isopropyl alcohol, the rate constant *k*<sub>H+N<sub>3</sub><sup>-</sup></sub> = 2.7 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> was obtained.<sup>39</sup> From the decrease of the yield of the hydrated electron by efficient electron scavengers, it was concluded that the reaction H• + e<sub>aq</sub><sup>-</sup> → H<sub>2</sub> + OH<sup>-</sup> contributes largely to the yield of H<sub>2</sub> in spurs.

In order to fit these results using Monte Carlo track chemistry simulations, two groups<sup>33,41</sup> concluded that “dry” secondary electrons, which serve as precursors to the “hydrated” electron (e<sub>aq</sub><sup>-</sup>), must be effectively scavenged by N<sub>3</sub><sup>-</sup> on the sub-picosecond timescale before hydration. This scavenging process was assumed to occur in the presence of a high concentration (>0.1–1 M) of azide ions (N<sub>3</sub><sup>-</sup>) in water. Emphasis was placed on the intriguing observation that this is an uncommon result because of the low reactivity of N<sub>3</sub><sup>-</sup> with e<sub>aq</sub><sup>-</sup>. Typically, quasi-free electrons are found to be scavenged by solutes known to be reactive towards hydrated electrons.<sup>42</sup> The authors did not discuss Peled's conclusions about the lack of reaction of prehydrated electrons.

The objective of the present study was to perform picosecond pulse radiolysis to observe directly if the dry electron (or quasi-free electron) reacts with N<sub>3</sub><sup>-</sup>. The quasi-free electron is involved in two reactions (4) and (8) for H<sub>2</sub> production in a short time. If the scavenging of a quasi-free electron occurs, that means: first, this is the first case where a hydrated electron does not react with a solute, but the quasi-free electron reacts very efficiently; second, the experiments of Peled *et al.* cannot be conclusive if N<sub>3</sub><sup>-</sup> scavenges both quasi-free electron and H• atom. Therefore, the experimental result with picosecond pulse radiolysis greatly impacts the hydrogen production mechanism.

## Experimental section

The formation and decay of the solvated electron were followed using the pulse radiolysis platform ELYSE – a laser-driven



Cs<sub>2</sub>Te photo-cathode (260 nm) accelerator (Paris-Saclay University), which utilizes short 5 ps pulses of electrons to produce, and 100 fs broad supercontinuum (350–1400 nm), to examine transient species.<sup>43,44</sup> The short electron pulses with a typical half-width of 5–7 ps, a charge of *ca.* 6 nC, and an energy of 7.8 MeV at a repetition rate of 5 Hz were utilized for experiments. The supercontinuum, generated by focusing a small part of the fundamental laser (780 nm) into a CaF<sub>2</sub> (350–780 nm) crystal, is split 50/50: probe/reference paths. Both probe and reference paths are coupled into optical fibers, transmitted to a spectrometer, and dispersed onto a cooled CCD camera (Andor Newton 920) for UV-vis detection. All kinetics presented in this work are calculated by averaging 3 transient maps with 6 electron pulses at each time delay step.

The formation yield of e<sub>hyd</sub> at just after the end of 5 ps electron pulse ( $G = 4.4 \times 10^{-7} \text{ M J}^{-1}$ ) correlates with the scavenging yield of a quasi-free electron. Less hydrated electron was formed if more quasi-free electrons were scavenged during the pulse.

## Results and discussion

Four solutions of NaN<sub>3</sub> with concentrations of 0.5, 1, 2, and 5 M, underwent investigation by observing hydrated electron kinetics within the 400 to 720 nm spectral range by pulse probe method (Fig. 1 top). A reference optical cell containing only

water determined the dose per pulse for each sample. Fig. 1 illustrates each concentration's time-dependent absorption spectra acquired through pulse probe measurements. The absorption spectra of the solvated electron exhibiting temporal variations, *i.e.*, blue-shift within the first 50 ps after of electron pulse, are particularly pronounced in the high-concentration azide solutions.

Selected absorption spectra at different time intervals for each solution are presented in Fig. 1 to emphasize the observed shifts. The observed changes over time are attributed to the formation of a pair in the presence of a high concentration of Na<sup>+</sup> and further solvation. At 5 M, the peak absorption shifts from 680 nm at the end of the electron pulse to 670 nm after 20 ps. Similar shifts are observed in 2 M but to a smaller extent. However, there is no detectable shift for the 0.1 M concentration, and the absorption band remains *ca.* 715 nm, the same as in water. The kinetics are reported for different samples at the absorption band maximum when an electron is fully solvated (Table 1), showing the solvated electron's stability during the first 100 ps. Except for the 0.1 M and 0.5 M solutions an increase in shorter wavelengths than 715 nm is observed just after the electron pulse. The shift of the absorption band of the solvated electron is very fast for a solution of 2 M N<sub>3</sub><sup>-</sup>, which is why we treated only the case of 5 M N<sub>3</sub><sup>-</sup> solution. Fig. 2 shows the dynamics of the solvation of electrons in 5 M azide solution by reporting the change of the maximum of the absorption band *versus* time. The data can be fitted with one exponential

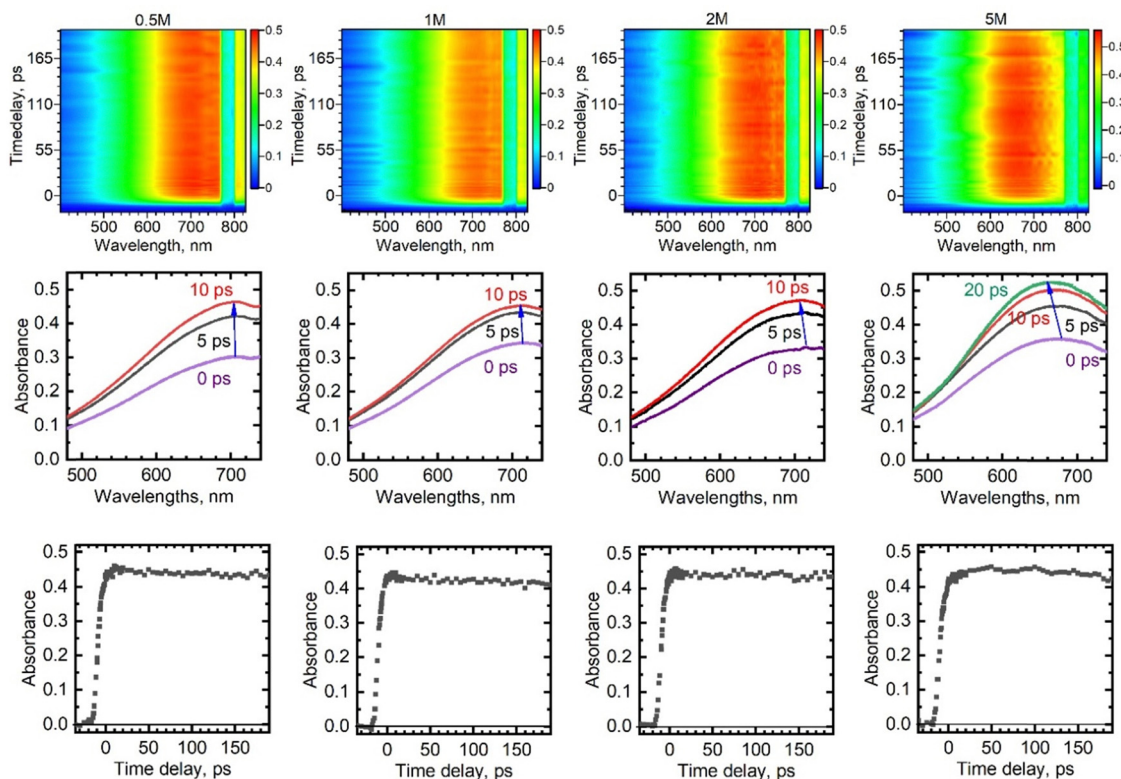
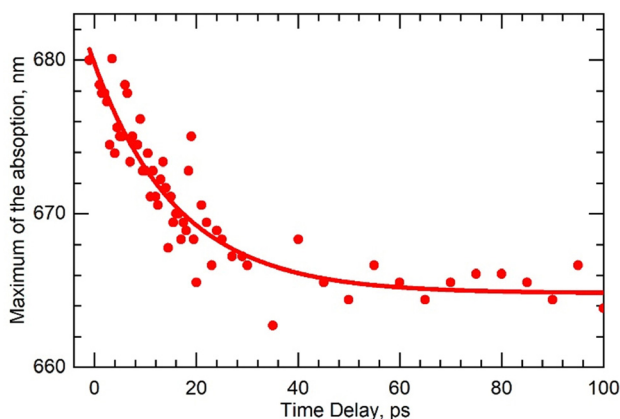


Fig. 1 Pulse probe measurements for different concentrations of N<sub>3</sub><sup>-</sup> in aqueous solutions. Top All spectral-kinetics data. The middle selected absorption band at different times, Bottom The kinetics observed at the maximum of the absorption band. Optical pathlength is 5 mm.



**Table 1** Solution density, estimated solvation time of electron, and the maximum for the absorption band of the solvated electron observed by pulse-probe measurements for each solution

NaN <sub>3</sub> concentration mol L <sup>-1</sup>	$\rho$ at 22 °C, g cm <sup>-3</sup> $\pm$ 0.005	$\lambda_{\text{max}}$ of the fully solvated electron $\pm$ 5 nm	Solvation time ps
0	1	715	< 1 ps
0.5	1	715	< 1 ps
1	1.03	712	A few ps
2	1.06	708	< 10 ps
5	1.18	670	16 ps



**Fig. 2** Change of the absorption band's maximum with time for the solution containing 5 M NaN<sub>3</sub>. The fit is a mono-exponential.

with a time constant of 16 ps. After 30 ps, the shape of the absorption spectra does not change and we can consider that the electron is fully solvated and paired with Na<sup>+</sup>.

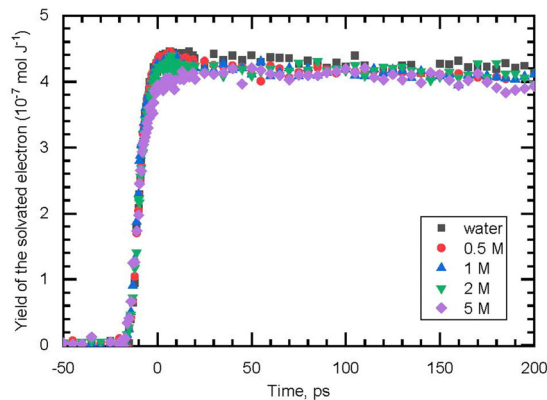
The kinetics at the absorption band's maximum when the spectra stabilize are depicted in Fig. 2. The observed absorption is more intense for the concentrated solution. This effect is due to the density of the solution. The values of the density  $\rho$  and  $\lambda_{\text{max}}$  are reported in Table 1.

Utilizing the dose per pulse ( $D$ ) for each sample and the same extinction coefficient,  $\varepsilon(\text{e}_{\text{hyd}}^-)$ , at the absorption band's maximum,  $\lambda_{\text{max}}$ , the time-dependent yield of the solvated electron,  $G_{\text{e}_{\text{aq}}^-}(t)$ , in various samples is deduced from the following equation:<sup>45</sup>

$$A(\lambda, t) = \varepsilon(\text{e}_{\text{aq}}^-) \cdot c(t) \cdot l = \varepsilon(\text{e}_{\text{aq}}^-) \cdot D \cdot G_{\text{e}_{\text{aq}}^-}(t) \cdot \rho \cdot l \quad (15)$$

Fig. 3 presents the time-dependent yield of the solvated electron for all solutions. The increase during the first 30 ps for 5 M solution is due to the absorption band shift. As shown, for all solutions 30 ps after the pulse, the yield is the same and equal to that of water. The results show clearly that even 5 M N<sub>3</sub><sup>-</sup> cannot scavenge the quasi-free electron. This experimental result does not agree with recent water radiolysis simulations to explain the yield of H<sub>2</sub>. In fact, from our observations, it is clear that, there is no reaction between the precursor of the solvated electron and N<sub>3</sub><sup>-</sup>.

It is beyond the scope of this paper to discuss Peled's results on the yield of H<sub>2</sub> further apart from to note that it must be



**Fig. 3** Time-dependent yield of the solvated electron in solutions containing N<sub>3</sub><sup>-</sup> at 0.5, 1, 2, and 5 M. The change during the first 30 ps is not due to the yield change but due to the solvation process.

concluded from their results that either H<sup>•</sup> is involved in the formation of a significant fraction of H<sub>2</sub> (*ca.* 50%) or N<sub>3</sub><sup>-</sup> is involved in some other mechanism apart from scavenging H<sup>•</sup> which suppresses H<sub>2</sub>. One possibility is hole scavenging, which is unlikely because high concentrations of Cl<sup>-</sup> do not affect the yield of H<sub>2</sub>.<sup>46</sup> There is the possibility that N<sub>3</sub><sup>-</sup> quenches excited states of water molecules, but this is unlikely to occur at the lower concentrations used in Peled's work. The use of very high concentrations such as 5 M azide, even if the purity of the reagent is high (such as 99% that we used), could, in Peled's experiment, have resulted in a fraction of solvated electrons being scavenged by impurities. However, he reported no change in yield at 100 ns. We performed pulse radiolysis in the microsecond range, and the decay of the solvated electron was observed for 1, 2, and 5 M azide solution. The decay is accelerated when the concentration of azide increases (Fig. 4). The observed rate constant is  $1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , which agrees with the previous value where only one concentration (1 M) was used for rate constant determination.<sup>39</sup>

This rate constant is low, and the solvated electron cannot be scavenged in the non-homogenous step. If  $\text{e}_{\text{aq}}^-$  does not react significantly with impurity, it can be concluded that reaction (11) is not involved in that component of H<sub>2</sub> production, which was suppressed in the study, which agrees with Bartels<sup>15</sup> conclusion based on yields in high-temperature water. Finally, the precise values for  $G(\text{H}_2)$  at high concentrations of azide (> 1 M) reported by Peled should be treated with caution because the calculated value depends on dosimetry in concentrated solutions. Peled chose to use the total dose corrected for solute, but if some of the H<sub>2</sub> arises from reaction (5), then it might be expected that only the dose to the water fraction should be considered, and that would result in an increase in  $G(\text{H}_2)$  in Peled's results which would suggest  $G(\text{H}_2)$  in azide solutions decreases to a steady value with increasing azide concentration above 4 M.

It is important to note that contrary to the case of the scavengers used in previous works (such as SeO<sub>4</sub><sup>2-</sup>, MoO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, and H<sub>2</sub>O<sub>2</sub>), which react very rapidly with the hydrated electron, the specific case of N<sub>3</sub><sup>-</sup> is



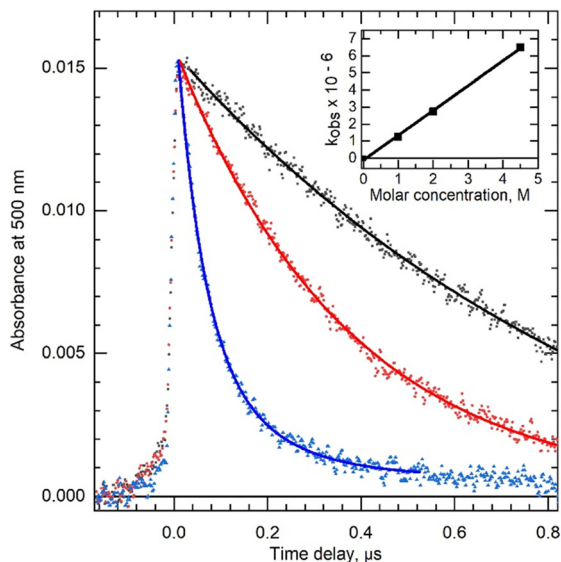


Fig. 4 Decay of the solvated electron was observed at 500 nm in azide solution with 1, 2, and 5 M concentrations. Optical pathlength is 5 mm. Inset, the pseudo-first-order rate constant versus  $N_3^-$  concentration.

that its reaction with the hydrated electron is very slow. In general, stochastic models simulate the effects of prehydrated electron scavengers on  $H_2$  yield well, for example, with  $NO_3^-$ ,<sup>41</sup> typifying most of the species listed by Pastina *et al.*<sup>4</sup> However, where the chemistry becomes more complex, for example, when  $Cu^{2+}$  is used, the model is less good and with no prehydrated electron scavenger,  $N_3^-$ , the model fails. In later work, Horne *et al.*<sup>11</sup> required the quenching by  $NO_3^-$  of  $H_2O^*$  formed by direct excitation, which occurred at the same rate as the reaction of  $e_{pre}^-$ . A problem for models is that there is no direct chemical evidence for the mechanisms, which ultimately involve the decomposition of excited states to form  $H_2$  at sub-picosecond timescales.

We can assume that the high concentration of  $Na^+$  does not affect the yield of  $H_2$ .  $H_3O^+$  forms an ion pair with  $e_{pre}^-$  similar to  $Na^+$ , which was included in a stochastic model for reactions of silver, and it was concluded that this ion pair reacted with  $Ag^+$  at the same rate as  $e_{pre}^-$ .<sup>47</sup>

Finally, we note that in our previous measurements in the presence of silver ion, it was shown that within experimental error, the sum of the yields of a silver atom and that of hydrated electron rose only slightly with increasing silver concentration, showing that the quasi-free electron mainly solvates in water.<sup>47</sup>

## Conclusions

It is concluded that the quasi-free electron does not react with  $N_3^-$  in agreement with the conclusions of Peled and in disagreement with assumptions used in stochastic models. In these concentrated solutions, the electron hydrates and rapidly forms an ion pair with  $Na^+$  resulting in a spectral shift as observed previously with  $H_3O^+$ .

If the sole effect of  $N_3^-$  is to scavenge  $H^\bullet$ , then the decrease in the yield of  $H_2$  measured by Peled must involve reactions of  $H^\bullet$  and rule out reaction (11), it can be concluded that if reactions (4) and (5) are important for the formation of part of the  $H_2$  yield, then only efficient quasi-free electron scavengers can suppress the  $H_2$  yield from this process.

Finally, because stochastic models require the reaction of quasi-free electrons with  $N_3^-$ , these models must be reassessed.

## Conflicts of interest

There are no conflicts to declare.

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