Reactivity of quasi-free electrons toward N_3^- and its impact on H_2 formation mechanism in water radiolysis

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Picosecond pulse radiolysis measurements were employed to assess the effectiveness of N_3^- in scavenging quasi-free electrons in aqueous solutions. The absorption on spectra of hydrated electrons were recorded within a 100 ps timeframe across four distinct solutions with 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, 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 H_2 formation in water radiolysis, which we discuss briefly here.

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 H_2 evolution.[1,2] 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.[3–7] It is generally assumed that when exposed to ionizing radiation, water molecules undergo ionizations and excitations:

$$H_2O \leadsto H_2O^{\bullet+} + e^- \text{ (ionization)} \qquad (1)$$

$$H_2O \leadsto H_2O^* \text{ (direct excitation)}, \qquad (2)$$
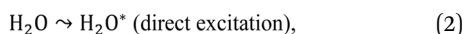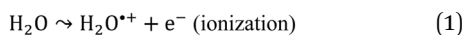
After being generated by radiation, the excess electron undergoes a solvation process, quickly becoming fully solvated in water within 1 picosecond, having a broad absorption band, peaking at 715 nm.

The electron can be hydrated in less than 1 ps:

$$e^- \rightarrow e_s^- \qquad (3)$$

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 e_{aq}^-. However, in solutions containing high concentrations of non-reactive metal cations like Na^+, which can interact with the electron, the symbol 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 e_s^-, $H^\bullet$, $^\bullet OH$, H_2, H_2O_2.[2,8,9]

Among these radiolysis products, one of the most interesting is molecular hydrogen, 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[4,5] in conjunction with computer simulations[3,10] have suggested that the majority of the total H_2 yield in ^{60}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 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 $H_2O^{\bullet+}$ parent cation (or "hole") due to their Coulomb attraction, which tends to draw them back together:[11–15]
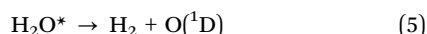
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$$H_2O^{\bullet+} + e^- \rightarrow H_2O^* \qquad (4)$$
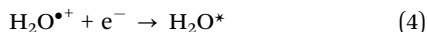
followed by the dissociation of the excited water molecule

$$H_2O^* \rightarrow H_2 + O(^1D) \qquad (5)$$

where $O(^1D)$ is the oxygen atom in its singlet state. Note that reaction (4) must take place before the $H_2O^{\bullet+}$ cation whose lifetime is less than a few tens of fs[16,17] undergoes proton transfer to a neighboring water molecule to give the hydronium cation H_3O^+ and the hydroxyl radical $^\bullet OH$.

$$H_2O^{\bullet+} + H_2O \rightarrow H_3O^+ + {}^\bullet OH \qquad (6)$$
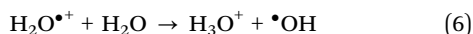
Since reaction (6) is ultrafast, reaction (4) can only involve the quasi-free electrons formed in the vicinity of the parent water cation and occurs in the first steps of their random walk, i.e., in times as short as a few femtoseconds.

(2) Decomposition of H_2O^* formed by direct excitation[4,11,18–22]

The excited state of water usually undergoes dissociation by forming $^\bullet OH$ and $^\bullet H$ radicals. However, another channel is considered for the dissociation process by forming H_2 according to the following reaction:

$$H_2O^* \rightarrow H_2 + {}^\bullet O \qquad (7)$$

(3) The "dissociative electron attachment" (or DEA) involves the resonant capture of a low-kinetic energy electron by a water molecule:[23–27]

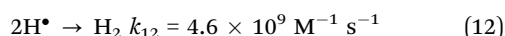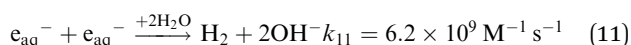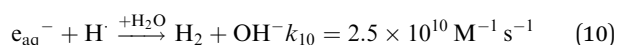$$H_2O + e^- \rightarrow H_2O^{*-} \rightarrow H^- + {}^\bullet OH \qquad (8)$$
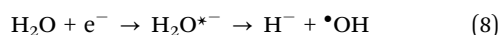
followed by the reaction of the hydride anion with a second water molecule via ultrafast proton transfer:

$$H^- + H_2O \rightarrow H_2 + OH^- \qquad (9)$$

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

(4) The residual production of H_2 through radiolysis is attributed to three specific radical–radical combination reactions involving the hydrated electron and $H^\bullet$ atom.[15,23,28–30] These reactions occur within the expanding tracks via diffusion during the nonhomogeneous chemical stage.

$$e_{aq}^- + H^\bullet \xrightarrow{+H_2O} H_2 + OH^- \quad k_{10} = 2.5 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (10)$$

$$e_{aq}^- + e_{aq}^- \xrightarrow{+2H_2O} H_2 + 2OH^- \quad k_{11} = 6.2 \times 10^9\ M^{-1}\ s^{-1} \qquad (11)$$

$$2H^\bullet \rightarrow H_2 \quad k_{12} = 4.6 \times 10^9\ M^{-1}\ s^{-1} \qquad (12)$$

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

Azides, N_3^-, consisting of three nitrogen atoms arranged linearly, are known for their reactivity and have applications in various fields.[31] The simplest azide is N_3^- anion, which is very soluble in water.[32] N_3^- can undergo radiolysis when exposed to ionizing radiation in aqueous solution.[33] It is well-known that azide reacts with $OH^\bullet$ radical, forming the azide radical:[34,35]

$$N_3^- + {}^\bullet OH \rightarrow N_3^\bullet \qquad (13)$$
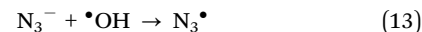
The radical $N_3^\bullet$ is a less oxidizing species than $OH^\bullet$ radical and is used as a one electron oxidizing radical.[36,37] In contrast, the hydrated electron reaction with N_3^- is very slow, and the value of the rate constant of this reaction is estimated to be lower than $1.5 \times 10^6\ M^{-1}\ s^{-1}$.[38,39] However, the reaction of N_3^- with $H^\bullet$ atom is fast with a rate constant of $k = 2.5 \times 10^9\ M^{-1}\ s^{-1}$:[40]

$$N_3^- + H^\bullet \rightarrow products \qquad (14)$$
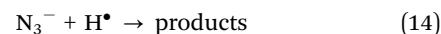
The slow reaction with the hydrated electron and the fast reaction with the $H^\bullet$ atom allows N_3^- as a selective scavenger to deduce information about the mechanism of H_2 formation. Peled et al.[39] showed that N_3^- reduces the yield of H_2, $G(H_2)$, from $0.45 \times 10^{-7}\ mol\ J^{-1}$ to 0.157 at 5 M N_3^- in neutral solutions and from 0.37 mol J^{-1} in 0.5 M solution to 0.21 mol J^{-1} at 4 M N_3^- in alkaline solutions. The hydrated electron reacts with azide very slowly, and the presence of 1 M N_3^- was found not to affect the solvated electron spectrum at 100 ns in their work.

In competition experiments between N_3^- and isopropyl alcohol, the rate constant $k_{H+N_3^-} = 2.7 \times 10^9\ M^{-1}\ s^{-1}$ was obtained.[39] From the decrease of the yield of the hydrated electron by efficient electron scavengers, it was concluded that the reaction $H^\bullet + e_{aq}^- \rightarrow H_2 + OH^-$ contributes largely to the yield of H_2 in spurs.

In order to fit these results using Monte Carlo track chemistry simulations, two groups[33,41] concluded that "dry" secondary electrons, which serve as precursors to the "hydrated" electron (e_{aq}^-), must be effectively scavenged by N_3^- 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_3^-) in water. Emphasis was placed on the intriguing observation that this is an uncommon result because of the low reactivity of N_3^- with e_{aq}^-. Typically, quasi-free electrons are found to be scavenged by solutes known to be reactive towards hydrated electrons.[42] 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_3^-. The quasi-free electron is involved in two reactions (4) and (8) for H_2 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_3^- scavenges both quasi-free electron and $H^\bullet$ 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$_2$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.[43,44] 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$_2$ (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$_{hyd}$ at just after the end of 5 ps electron pulse ($G = 4.4 \times 10^{-7}$ 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$_3$ 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$^+$ 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$_3^-$, which is why we treated only the case of 5 M N$_3^-$ 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
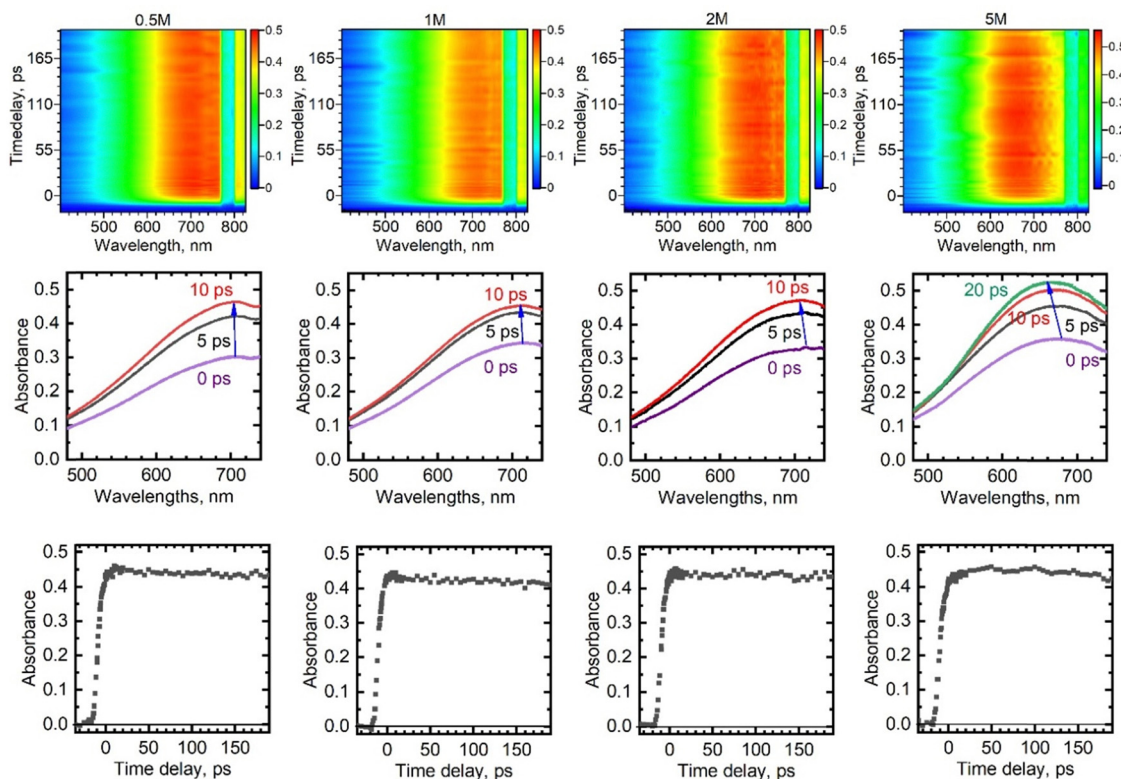

Fig. 1 Pulse probe measurements for different concentrations of N$_3^-$ in aqueous solutions. Top All spectral-kinetics data. The middle selected absorption band at different times, Bottom The kinetics observed at the maximum of the absorption band. Optical pathlength is 5 mm.

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

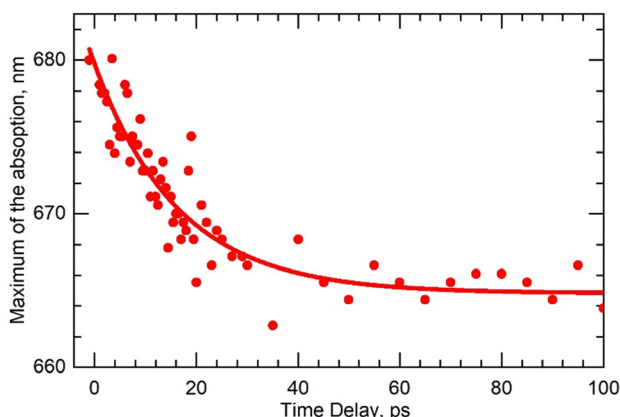| NaN$_3$ concentration mol L^{-1}	ρ at 22 °C, g cm^{-3} ± 0.005	λ_{max} of the fully solvated electron ± 5 nm	Solvation time ps
0	1	715	<1 ps
0.5	1	715	<1 ps
1	1.03	712	A few ps
2	1.06	708	<10 ps
5	1.18	670	16 ps

Fig. 2 Change of the absorption band's maximum with time for the solution containing 5 M NaN$_3$. 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$^+$.

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 ρ and λ_{max} are reported in Table 1.

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

$$A(\lambda, t) = \varepsilon(e_{aq}^-)\cdot c(t)\cdot l = \varepsilon(e_{aq}^-)\cdot D\cdot G_{e_{aq}^-}(t)\cdot \rho\cdot l \qquad (15)$$

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$_3^-$ cannot scavenge the quasi-free electron. This experimental result does not agree with recent water radiolysis simulations to explain the yield of H$_2$. In fact, from our observations, it is clear that, there is no reaction between the precursor of the solvated electron and N$_3^-$.

It is beyond the scope of this paper to discuss Peled's results on the yield of H$_2$ further apart from to note that it must be
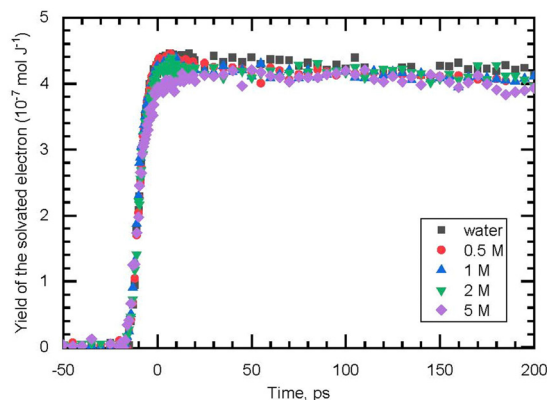

Fig. 3 Time-dependent yield of the solvated electron in solutions containing N$_3^-$ at 0.5, 1, 2, and 5 M. The change during the first 30 ps is not due to the yield change but due to the solvation process.

concluded from their results that either H$^\bullet$ is involved in the formation of a significant fraction of H$_2$ (*ca.* 50%) or N$_3^-$ is involved in some other mechanism apart from scavenging H$^\bullet$ which suppresses H$_2$. One possibility is hole scavenging, which is unlikely because high concentrations of Cl$^-$ do not affect the yield of H$_2$.[46] There is the possibility that N$_3^-$ 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 1.4×10^6 M^{-1} s^{-1}, which agrees with the previous value where only one concentration (1 M) was used for rate constant determination.[39]

This rate constant is low, and the solvated electron cannot be scavenged in the non-homogenous step. If e$^-_{aq}$ does not react significantly with impurity, it can be concluded that reaction (11) is not involved in that component of H$_2$ production, which was suppressed in the study, which agrees with Bartels[15] conclusion based on yields in high-temperature water. Finally, the precise values for $G(H_2)$ 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$_2$ 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 $G(H_2)$ in Peled's results which would suggest $G(H_2)$ 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$_4^{2-}$, MoO$_4^{2-}$, Cr$_2$O$_7^{2-}$, NO$_2^-$, NO$_3^-$, Cd^{2+}, Cu^{2+}, and H$_2$O$_2$), which react very rapidly with the hydrated electron, the specific case of N$_3^-$ is

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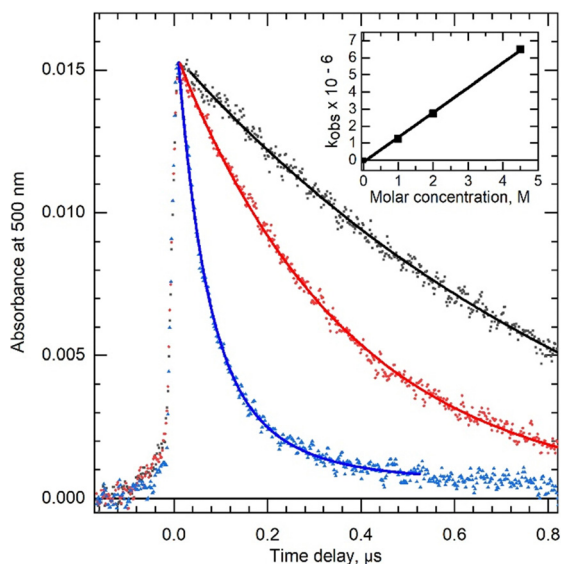*Phys. Chem. Chem. Phys.*, 2024, **26**, 11604–11610 | **11607**

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^-,[41] typifying most of the species listed by Pastina *et al.*[4] 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.*[11] 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}^-.[47]

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.[47]

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.

References

1 G. Buxton, The Radiation Chemistry of Liquid Water, *Charged Particle and Photon Interactions with Matter*, CRC Press, 2003.

2 J. V. Belloni, M. Mostafavi, T. Douki and M. Spotheim-Maurizot, *Radiation chemistry from basics to applications in material and life sciences*, EDP Sciences, 2008.

3 H. A. Schwarz, Applications of the spur diffusion model to the radiation chemistry of aqueous solutions, *J. Phys. Chem.*, 1969, **73**(6), 1928–1937.

4 B. Pastina, J. A. LaVerne and S. M. Pimblott, Dependence of Molecular Hydrogen Formation in Water on Scavengers of the Precursor to the Hydrated Electron, *J. Phys. Chem. A*, 1999, **103**(29), 5841–5846.

5 V. M. Byakov, The nature of the precursors of radiolytic molecular hydrogen in water, and the mechanism of positronium formation in liquids, *Int. J. Radiat. Phys. Chem.*, 1976, **8**(3), 283–288.

6 J. M. Wiesenfeld and E. P. Ippen, Dynamics of electron solvation in liquid water, *Chem. Phys. Lett.*, 1980, **73**(1), 47–50.

7 W. J. Chase and J. W. Hunt, Solvation time of the electron in polar liquids. Water and alcohols, *J. Phys. Chem.*, 1975, **79**(26), 2835–2845.

8 H. Morawetz, Radiation chemistry-principles and applications, Farhataziz and Michael A. J. Rodgers, Eds. VCH, New York and Germany, 1987, 641 pp. Price, *J. Polym. Sci., Part C: Polym. Lett.*, 1987, **25**(12), 510.

9 J. Meesungnoen, S. Sanguanmith and J. P. Jay-Gerin, Yields of H_2 and hydrated electrons in low-LET radiolysis of water determined by Monte Carlo track chemistry simulations using phenol/N_2O aqueous solutions up to 350 °C, *RSC Adv.*, 2015, **5**(94), 76813–76824.

10 W. G. Burns, H. E. Sims and J. A. B. Goodall, Radiation chemical diffusion kinetic calculations with prescribed and non-prescribed diffusion—I, *Radiat. Phys. Chem.*, 1984, **23**(1–2), 143–180.

11 G. P. Horne, S. M. Pimblott and J. A. LaVerne, Inhibition of Radiolytic Molecular Hydrogen Formation by Quenching of Excited State Water, *J. Phys. Chem. B*, 2017, **121**(21), 5385–5390.

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12 S. Sanguanmith, J. Meesungnoen, Y. Muroya and J. P. Jay-Gerin, Scavenging of ''dry'' electrons prior to hydration by azide ions: effect on the formation of H$_2$ in the radiolysis of water by ^{60}Co γ-rays and tritium β-electrons, *Can. J. Chem.*, 2021, **99**(11), 881–889.

13 R. L. Platzman, Subexcitation Electrons, *Radiat. Res.*, 1955, **2**(1), 1.

14 V. Cobut, J. P. Jay-Gerin, Y. Frongillo and J. P. Patau, On the dissociative electron attachment as a potential source of molecular hydrogen in irradiated liquid water, *Radiat. Phys. Chem.*, 1996, **47**(2), 247–250.

15 D. Janik, I. Janik and D. M. Bartels, Neutron and β/γ Radiolysis of Water up to Supercritical Conditions. 1. β/γ Yields for H$_2$, H$^•$ Atom, and Hydrated Electron, *J. Phys. Chem. A*, 2007, **111**(32), 7777–7786.

16 M. F. Lin, N. Singh, S. Liang, M. Mo, J. P. F. Nunes and K. Ledbetter, *et al.*, Imaging the short-lived hydroxyl-hydronium pair in ionized liquid water, *Science*, 2021, **374**(6563), 92–95.

17 Z. H. Loh, G. Doumy, C. Arnold, L. Kjellsson, S. H. Southworth and A. Al Haddad, *et al.*, Observation of the fastest chemical processes in the radiolysis of water, *Science*, 2020, **367**(6474), 179–182.

18 G. R. Sunaryo, Y. Katsumura, D. Hiroishi and K. Ishigure, Radiolysis of water at elevated temperatures—II. Irradiation with γ-rays and fast neutrons up to 250 °C, *Radiat. Phys. Chem.*, 1995, **45**(1), 131–139.

19 D. Swiatla-Wojcik and G. V. Buxton, Modeling of radiation spur processes in water at temperatures up to 300.degree, *J. Phys. Chem.*, 1995, **99**(29), 11464–11471.

20 W. G. Burns and W. R. Marsh, Radiation chemistry of high-temperature (300–410 °C) water. Part 1.—Reducing products from gamma radiolysis, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**(1), 197.

21 C. Lifshitz, Isotope Effects in X-ray-Irradiated Acidified H$_2$O–D$_2$O Solutions, *Can. J. Chem.*, 1963, **41**(9), 2175–2186.

22 S. Rose′n, A. Derkatch, J. Semaniak, A. Neau, A. Al-Khalili and A. Le Padellec, *et al.*, Recombination of simple molecular ions studied in storage ring: dissociative recombination of H$_2$O$^+$, *Faraday Discuss.*, 2000, **115**, 295–302.

23 M. Sterniczuk and D. M. Bartels, Source of Molecular Hydrogen in High-Temperature Water Radiolysis, *J. Phys. Chem. A*, 2016, **120**(2), 200–209.

24 M. G. Curtis and I. C. Walker, Dissociative electron attachment in water and methanol (5–14 eV), *J. Chem. Soc., Faraday Trans.*, 1992, **88**(19), 2805–2810.

25 C. E. Melton, Cross Sections and Interpretation of Dissociative Attachment Reactions Producing OH−, O−, and H− in H$_2$O, *J. Chem. Phys.*, 1972, **57**(10), 4218–4225.

26 C. E. Melton and G. A. Neece, Rate constants and cross sections for the production of OH- from O- and H- in water, *J. Am. Chem. Soc.*, 1971, **93**(25), 6757–6759.

27 J. Ma, F. Wang and M. Mostafavi, Ultrafast Chemistry of Water Radical Cation, H$_2$O$^{•+}$, in Aqueous Solutions, *Molecules*, 2018, **23**(2), 244.

28 G. A. Kimmel, T. M. Orlando, C. Vézina and L. Sanche, Low-energy electron-stimulated production of molecular hydrogen from amorphous water ice, *J. Chem. Phys.*, 1994, **101**(4), 3282–3286.

29 M. Faraggi, D. Zehavi and M. Anbar, Effect of thallous ions on the yields of hydrogen and hydrogen peroxide in radiolyzed aqueous solutions, *Trans. Faraday Soc.*, 1971, **67**, 2057.

30 V. Cobut, J. P. Jay-Gerin, Y. Frongillo and J. P. Patau, On the dissociative electron attachment as a potential source of molecular hydrogen in irradiated liquid water, *Radiat. Phys. Chem.*, 1996, **47**(2), 247–250.

31 S. Bräse, C. Gil, K. Knepper and V. Zimmermann, Organic Azides: An Exploding Diversity of a Unique Class of Compounds, *Angew. Chem., Int. Ed.*, 2005, **44**(33), 5188–5240.

32 K. Turnbull, B. Narsaiah, J. S. Yadav, T. Yakaiah and B. P. V. Lingaiah, Sodium Azide, *Encyclopedia of Reagents for Organic Synthesis. Chichester*, John Wiley & Sons, Ltd, UK, 2008.

33 S. Sanguanmith, J. Meesungnoen, Y. Muroya and J. P. Jay-Gerin, Scavenging of ''dry'' electrons prior to hydration by azide ions: effect on the formation of H$_2$ in the radiolysis of water by ^{60}Co γ-rays and tritium β-electrons, *Can. J. Chem.*, 2021, **99**(11), 881–889.

34 G. R. Dey, Nitrite formation in aerated aqueous azide solutions: A radiation chemical study, *Res. Chem. Intermed.*, 2007, **33**(7), 599–611.

35 A. T. Al-Kazwini, P. O'Neill, G. E. Adams, R. B. Cundall, G. Lang and A. Junino, Reactions of indolic radicals produced upon one-electron oxidation of 5,6-dihydroxyindole and its N(1)-methylated analogue, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1941.

36 S. Sanguanmith, J. Meesungnoen, C. R. Stuart, P. Causey and J. P. Jay-Gerin, Self-radiolysis of tritiated water. 4. The scavenging effect of azide ions (N3−) on the molecular hydrogen yield in the radiolysis of water by ^{60}Co γ-rays and tritium β-particles at room temperature, *RSC Adv.*, 2018, **8**(5), 2449–2458.

37 C. Lambert, T. G. Truscott, E. J. Land and P. A. Riley, Role of azide concentration in pulse radiolysis studies of oxidation: 3,4-dihydroxyphenylalanine, *J. Chem. Soc., Faraday Trans.*, 1991, **87**(18), 2939.

38 B. Smaller, E. C. Avery and J. R. Remko, EPR Pulse Radiolysis Studies of the Hydrogen Atom in Aqueous Solution. I. Reactivity of the Hydrogen Atom, *J. Chem. Phys.*, 1971, **55**(5), 2414–2418.

39 E. Peled, U. Mirski and G. Czapski, Contribution of hydrogen atoms to GH2 in the radiation chemistry of aqueous solutions, *J. Phys. Chem.*, 1971, **75**(1), 31–35.

40 D. J. Deeble, B. J. Parsons and G. R. Alastair Johnson, Reactions of the hydrogen atom with azide, bromide and iodide ions in aqueous solution, *Int. J. Radiat. Appl. Instrum., Part C*, 1990, **36**(3), 487–491.

41 R. E. Harris and S. M. Pimblott, On 3H β-particle and ^{60}Co γ irradiation of aqueous systems, *Radiat. Res.*, 2002, **158**(4), 493–504.

42 C. D. Jonah, J. R. Miller and M. S. Matheson, The reaction of the precursor of the hydrated electron with electron scavengers, *J. Phys. Chem.*, 1977, **81**(17), 1618–1622.

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Phys. Chem. Chem. Phys., 2024, **26**, 11604–11610 | **11609**

43 J. Belloni, H. Monard, F. Gobert, J. P. Larbre, A. Demarque and V. De Waele, *et al.*, ELYSE - A picosecond electron accelerator for pulse radiolysis research, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 2005, 527–539.

44 J. L. Marignier, V. de Waele, H. Monard, F. Gobert, J. P. Larbre and A. Demarque, *et al.*, Time-resolved spectroscopy at the picosecond laser-triggered electron accelerator ELYSE, *Radiat. Phys. Chem.*, 2006, **75**(9), 1024–1033.

45 F. Wang, U. Schmidhammer, J. P. Larbre, Z. Zong, J. L. Marignier and M. Mostafavi, Time-dependent yield of the hydrated electron and the hydroxyl radical in D_2O: a picosecond pulse radiolysis study, *Phys. Chem. Chem. Phys.*, 2018, **20**(23), 15671–15679.

46 A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, Decomposition of Water and Aqueous Solutions under Mixed Fast Neutron and γ-Radiation, *J. Phys. Chem.*, 1952, **56**(5), 575–586.

47 A. Balcerzyk, U. Schmidhammer, G. Horne, F. Wang, J. Ma and S. M. Pimblott, *et al.*, Unexpected Ultrafast Silver Ion Reduction: Dynamics Driven by the Solvent Structure, *J. Phys. Chem. B*, 2015, **119**(31), 10096–10101.

11610 | *Phys. Chem. Chem. Phys.*, 2024, **26**, 11604–11610

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