MONTE-CARLO SIMULATION OF THE LOW-LET RADIOLYSIS OF LIQUID WATER OVER THE RANGE 25 TO 350°C

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Abstract

A re-examination of our Monte-Carlo modeling of the high-temperature radiolysis of liquid water by low linear energy transfer (LET ~ 0.3 keV/µm) radiation was undertaken in an attempt to reconcile our computed *g*-values (primary or "escape" yields) of the various radiolytic products (e^{-}_{aq}, $^{\bullet}OH$, $H^{\bullet}$, H_2, and H_2O_2) with newly measured or recently re-assessed experimental data over the range from 25 up to 350°C. In the calculations, we used the radiolysis database, including the rate constants, the diffusion coefficients of the radiation-induced species, the reaction mechanisms and the *g*-values, recently collected and summarized by Elliot (AECL) and Bartels (University of Notre Dame). Using a global-fit procedure, experimental data were found to be best reproduced when a discontinuity in the temperature dependence of certain physicochemical parameters was introduced at ~100-150°C. The presence of such a discontinuity was hypothesized to be associated with a change in the liquid structure of water around these temperatures. In addition to the physicochemical factors intervening in the radiolysis, the importance of the reaction of $H^{\bullet}$ atoms with water in contributing to the unexplained yield of H_2 above 200°C was also investigated.

1. Introduction

The radiolysis of liquid water at elevated temperatures is a subject of considerable interest to nuclear power engineers. In boiling water reactors (BWR) and pressurized water reactors (PWR), the nuclear core is cooled by liquid water that is typically at a temperature in the range of 285-320°C. The aqueous coolant undergoes radiolytic decomposition induced by an intense ionizing radiation field in the core, comprising low linear energy transfer (LET) γ-rays and fast neutrons whose energy is transferred to protons and oxygen nuclei resulting in the emission of charged particle recoils of high LET. The aqueous radiolysis products must be assessed because they can induce deleterious corrosion, hydriding, and cracking of sensitive materials both in the core and in the various piping components of the reactors [1-4]. The basic interest of nuclear power engineers is to know the real concentrations of the oxidizing products and to select conditions at which their formation could be suppressed. However, direct measurement of the chemistry in reactor cores is extremely difficult. The extreme conditions of high temperature, pressure, and mixed neutron/gamma radiation fields are, of course, not compatible with normal chemical instrumentation. For these reasons, theoretical models and computer simulations are an important route of investigation to predict the detailed radiation chemistry of the cooling water in the core and the consequences for materials [5,6].

In this work, we re-examine our Monte-Carlo modeling of the high temperature radiolysis of liquid water by low LET radiation [7], in an attempt to reconcile our computed primary yields (or *g*-values)[1] of the various radiolytic products with newly measured or recently re-assessed experimental data up to 350°C. Much of the data required to model this radiolysis, including reaction rate constants, diffusion coefficients of the radiation-induced species, reaction mechanisms, and *g*-values, are drawn from a recent compilation by Elliot and Bartels [8]. Specifically, we use a global-fit procedure, which consists of *simultaneously* fitting all our computed temperature-dependent *g*-values to the available experimental data, to re-evaluate the values of certain adjustable parameters that intervene in the physicochemical stage of the radiolysis. These parameters include, in particular, the thermalization distance (r_{th}) and the dissociative attachment (DEA) of subexcitation electrons,[2] and the branching ratios of the excited water molecule decay channels.

2. Monte-Carlo simulations

Monte-Carlo techniques are used to model the complex succession of events that are generated in liquid water under irradiation. A detailed description and implementation of our Monte-Carlo code IONLYS-IRT that simulates, in a three-dimensional geometrical environment, the initial production of the various reactive species and the subsequent chemical reactions of these species have been given previously [7,10-13]. In brief, the IONLYS program models, on an event by event basis, all the events of the early "physical" ($<10^{-15}$ s) and "physicochemical" ($\sim10^{-15}$-10^{-12} s) stages in the track development. The complex spatial distribution of reactants at the end of the physicochemical stage, which is provided as an output of the IONLYS program, is then used directly as the starting point for the "nonhomogeneous chemical" stage (from $\sim10^{-12}$ s up to about 10^{-7}-10^{-6} s at 25°C). This third stage, during which the various radiolytic species diffuse randomly and react with one another (or with the environment) until all spur/track processes are complete (that is, at the end of spur/track expansion when the species have become homogeneously distributed in the bulk of the solution), is covered by our IRT program. This program employs the "independent reaction times" (IRT) method [14,15], a computer-efficient stochastic simulation technique that is used to simulate reaction times without having to follow the trajectories of the diffusing species. The IRT method relies on the approximation that the reaction time of each pair of reactants is independent of the presence of other reactants in the system. Within the framework of this approach, the competition between the reactions is simply described via a sorting out of the stochastically sampled reaction times for each of the potentially reactive pairs of reactants. The ability of our IRT program [11-13] to give accurate time-dependent chemical yields has been validated by comparison with full random flight Monte-Carlo simulations that do follow the reactant trajectories in detail [16].

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[1] Throughout this paper, *g*-values are given in the units of molecules per 100 eV (abbreviated molec./100 eV). For conversion into SI units (mol/J): 1 molec./100 eV ≈ 0.10364 μmol/J.

[2] Subexcitation electrons are those that have kinetic energies lower than the first electronic excitation threshold of the medium (~7.3 eV in liquid water). They lose energy relatively slowly, the dominant mode of energy loss being the excitation of molecular vibrations [9].

In the current paper, we use an extended version of our IONLYS-IRT Monte-Carlo simulation code [7,10-13] to examine the effect of temperature on the low-LET radiolysis[3] of liquid water in the range from ambient up to 350°C.[4] The important parameters are the yields of the primary products of water radiolysis and the rate constants of their inter-reactions. In this version of IONLYS-IRT, we use the radiolysis database, including the rate constants, the reaction mechanisms, and the *g*-values, recently compiled by Elliot and Bartels [8]. This new database provides a recommendation for the best values to use in high-temperature modeling of water radiolysis up to 350°C.

3. Results and discussion

3.1 Temperature dependence of the bimolecular self-reaction of the hydrated electron

Of particular significance, we have adopted in this work the temperature dependence of the rate constant for the self-reaction of e^{-}_{aq} as recently measured in *alkaline* water by Marin et al. [8,18]. Overall, this rate constant exhibits a similar behavior to those previously reported [19-21], namely, it increases with temperature in accordance with an Arrhenius relationship up to ~150°C and then decreases sharply as the temperature is further increased. The mechanism behind this inverse temperature dependence above 150°C is not understood, but it is generally thought to involve the formation of some transient intermediate [22], such as a hydride ion (H^{-}) or a hydrated electron dimer or dielectron ($e_2{}^{2-}{}_{aq}$) sharing the same solvent cavity [18,19,23,24]. The applicability of this abrupt drop in the rate constant above 150°C to *near-neutral* solution, however, has long been a subject of discussion on the pretext that it could be a function of the pH of the solution [25]. In fact, until recently, most computer modelers of the radiolysis of water at high temperatures have employed, in neutral solution, an extrapolation procedure previously proposed by Elliot [20], assuming that such an abrupt change does not occur and that this reaction is diffusion controlled at temperatures above 150°C. This assumption was justified mainly by the good agreement obtained between model and experiment [7,13,26].

Recently, Bartels and coworkers [8,18,27] emphasized that the measured temperature behavior of the rate of the bimolecular decay of e^{-}_{aq} in alkaline solution should in fact be regarded as *independent* of pH. Consequently, the incorporation of the drop in reaction rate at temperatures greater than ~150°C in the simulations leads, as predicted earlier [7,26,28], to a sharp downward discontinuity in $g(H_2)$, which is not observed experimentally (Fig. 1). To obtain acceptable fits of our calculated yields to the experimental data above 150°C, we were therefore led, in order to counterbalance the influence of the rate constant for the self-reaction of e^{-}_{aq}, to adjust the temperature dependence of certain parameters involved in the physicochemical stage of the radiolysis, namely, the electron thermalization distance (r_{th}), the dissociative electron attachment (DEA), and the branching ratios of the different excited water molecule decay channels.

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[3] To reproduce the effects of ^{60}Co γ-radiolysis, we use short track segments (~150 μm) of 300-MeV protons over which the average LET value obtained in the simulations is ~0.3 keV/μm at 25°C [1,11].

[4] All Monte-Carlo simulations reported here are performed along the liquid-vapor coexistence curve, the density of the pressurized water decreasing from 1 g/cm^3 (1 bar or 0.1 MPa) at 25° to 0.575 g/cm^3 (16.5 MPa) at 350°C [17]. For this range of temperature, calculations show that *g*-values are, to a large extent, essentially independent of the applied pressure.

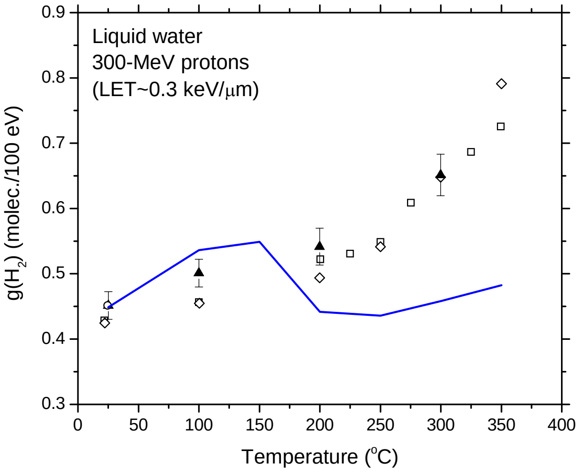

Figure 1: Influence of the self-reaction of e^-_{aq} on the primary yield of H_2 in the low-LET radiolysis of liquid water. The solid line shows our Monte-Carlo simulation results of $g(H_2)$ as a function of temperature, when the abrupt drop in the value of the rate constant for the self-reaction of e^-_{aq} above 150°C is incorporated in the calculations. As can be seen, $g(H_2)$ shows a marked inflection at ~150°C which is not observed experimentally. Symbols, representing experimental data, are from [5] (◇,□), [29] (▲), and [30] (○).

3.2 Temperature dependence of the thermalization distance of subexcitation electrons, DEA, and branching ratios of the excited water molecule decay channels

The values of r_{th} were obtained from comparing our computed time-dependent e^-_{aq} yield data to recent picosecond (~60 ps to 6 ns) and conventional nanosecond (using methyl viologen MV^{2+} scavenging of electrons) pulse radiolysis measurements of the decay kinetics of e^-_{aq} at several different temperatures between 25 and 350°C [31,32] (see Fig. 2).

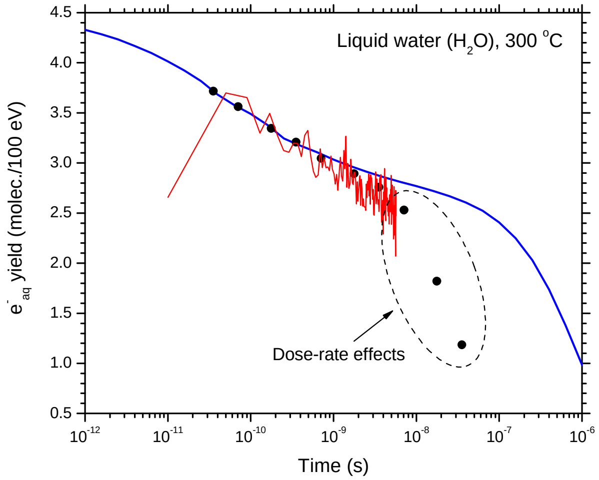

Figure 2: Comparison of the experimental fast decay kinetics of e^-_{aq} in water (H_2O) at 300°C and 25 MPa, with our Monte-Carlo simulation results. The value of r_{th} was obtained from a best fitting of the kinetic traces. The red line and the solid circles represent the experimental data obtained by direct picosecond pulse radiolysis (~60 ps to 6 ns, ~15 Gy/pulse) and by conventional nanosecond pulse radiolysis using e^-_{aq} scavenging by MV^{2+}, respectively [31,32].

Interestingly, fitting the kinetic traces was critically dependent on the selected value of r_{th}. Using this best fitting procedure over the temperature range studied, r_{th} is found to remain relatively unchanged below ~100-150°C (and equal to the r_{th} value at 25°C), but to decrease sharply at higher temperatures (Fig. 3). Noteworthy, r_{th}/r_{th}(25°C) at 300°C is equal to ~0.4, a value that is very close to that we adopted in our previous studies on the radiolysis of water at high temperatures [7,13,33]. Moreover, the observed *decrease* of r_{th} above 100-150°C is consistent with our previous work [7]. Physically, it indicates that there is an increase in the scattering cross sections of subexcitation electrons[5] that accounts for a decrease in the degree of structural order of water molecules due to an increasing breaking of hydrogen bonds with temperature. This also suggests that the effect resulting from this electron scattering mechanism prevails over that originating from a change in the initial spatial distribution of electrons in spurs due to the decrease in the density of the pressurized water. Note that this latter effect led Swiatla-Wojcik and Buxton [26], as well as LaVerne and Pimblott [28], to assume an increase in r_{th} at elevated temperature.

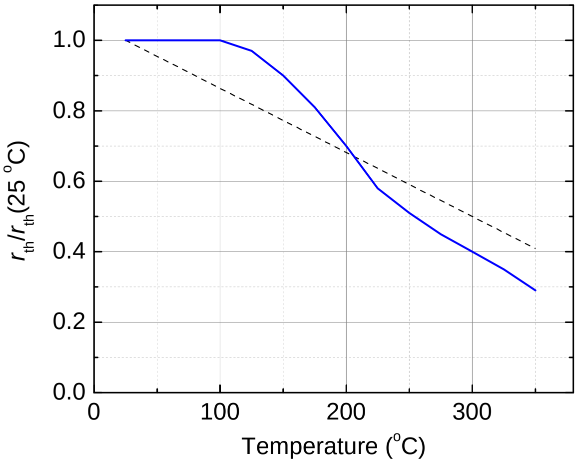

Figure 3: Temperature dependence of r_{th} over the range 25-350°C (solid line). The average electron thermalization distance at 25°C calculated from our simulations is r_{th}(25°C) ~ 11.7 nm [12]. The dashed line corresponds to the temperature dependence of r_{th} we adopted in our previous studies on the radiolysis of water at high temperatures [7,13,33].

The observation of a marked discontinuity of r_{th} around 100-150 °C is clearly a novel finding, tending to suggest that liquid water undergoes a rapid alteration in its local structural order or, equivalently, in its hydrogen bonding network, near these temperatures. Such a result is obviously of critical importance in our understanding and also the modeling of the radiation chemistry of water at high temperatures. It could, for example, shed new light on the mechanism by which the rate constant for the self-reaction of e^-_{aq} drops at temperatures above 150°C. The presence of such a loss of order in the molecular structure of water around 100-150°C does not

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[5] Electrons in the subexcitation energy range are known to be very sensitive to the structural order of the surrounding medium, owing to their non-negligible delocalized character. In various media, their scattering cross sections have been shown to increase rapidly when the degree of order diminishes [34].

seem to have been reported so far, although certain indications exist in the literature [35-37]. Work is planned to further investigate water's molecular geometry and the change in the intermolecular hydrogen bonding in this particular range of temperatures.

Building on our findings on r_{th}, we incorporated in our modeling calculations a dependence on temperature of the DEA and of the branching ratios of the different decay channels for excited water molecules in a form similar to that of r_{th} (Fig. 3), that is, with a marked discontinuity at ~100-150°C followed by a linear variation above ~250°C. In the absence of other detailed experimental information, we also assumed that their values at 350°C were equal to those observed in water *vapor*.[6] For example, the maximum value of the DEA cross section, adjusted to $\sim 2.85 \times 10^{-18}$ cm^2 at ~8.7 eV in order to reproduce the prompt (apparently) "nonscavengeable" yield of H_2 observed at room temperature [12], was set equal to its corresponding gas-phase value of 6.7×10^{-18} cm^2 [38] at 350°C. As for the branching ratios associated with the various channels through which the excited water molecules decay, they remain largely unknown in the liquid phase. Similarly, a temperature dependence incorporating a discontinuity around 100-150°C was included in the modeling for the decomposition of the different excited states of water, both electronic and vibrational. The contributions of these channels at 350°C were also assumed to be equal to those reported for the gas phase [10,12].

3.3 Temperature dependence of the *g*-values for e^-_{aq}, $^\bullet OH$, $H^\bullet$, H_2O_2, and H_2

The *g*-values of the various radiolytic products of the low-LET radiolysis of water, calculated at the end of spur expansion[7] from our Monte-Carlo simulations, are compared with most recent experimental data in Fig. 4a-e. In the calculations, we used, as described above, the self-consistent radiolysis database recently compiled by Elliot and Bartels [8]. As shown in Fig. 4, a good overall agreement is found between calculated and experimental yields up to 350°C. Most importantly, experimental yields were found to be best reproduced *simultaneously* when a discontinuity in the temperature dependence of r_{th}, DEA, and the branching ratios of the excited water molecule decay channels was introduced at ~100-150°C. In particular, the sharp downward discontinuity predicted for $g(H_2)$ at 150°C (Fig. 1) is no longer apparent (Fig. 4e).

With the exception of $g(H_2)$, all calculated *g*-values are consistent with the general observation that when the temperature is increased, the yields of "free radicals" $g(e^-_{aq})$, $g(^\bullet OH)$, and $g(H^\bullet)$ continuously increase while the "molecular" yield $g(H_2O_2)$ decreases. Although H_2 is a molecular product, $g(H_2)$ was observed to continue to increase with temperature, particularly above 200°C. This anomalous increase in $g(H_2)$ is briefly discussed below (see Sect. 3.4). The general trend of having yields of free radicals that increase with temperature can readily be explained from the fact that many important recombination reactions in the spur are not diffusion-controlled and therefore have rate constants that increase *less* with temperature than do the diffusion of the

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[6] A depleted hydrogen bonding in the liquid with increasing temperature is consistent with a change in those parameters towards their observed *gas-phase* values [26].

[7] The lifetime (τ_s) of the spur is an important indicator for overlapping spurs, giving the time required for the changeover from spur kinetics to homogeneous kinetics in the bulk solution. τ_s and its temperature dependence have been determined recently. Calculations show that τ_s decreases by about an order of magnitude over the 25-350°C temperature range, going from $\sim 4.2 \times 10^{-7}$ s at 25°C to $\sim 5.7 \times 10^{-8}$ s at 350°C [39].

individual species out of the spur [7,20,29,40]. In other words, as the temperature increases, diffusion of the radical species out of the spur increases more rapidly than recombination, and one should have less molecular recombination products.

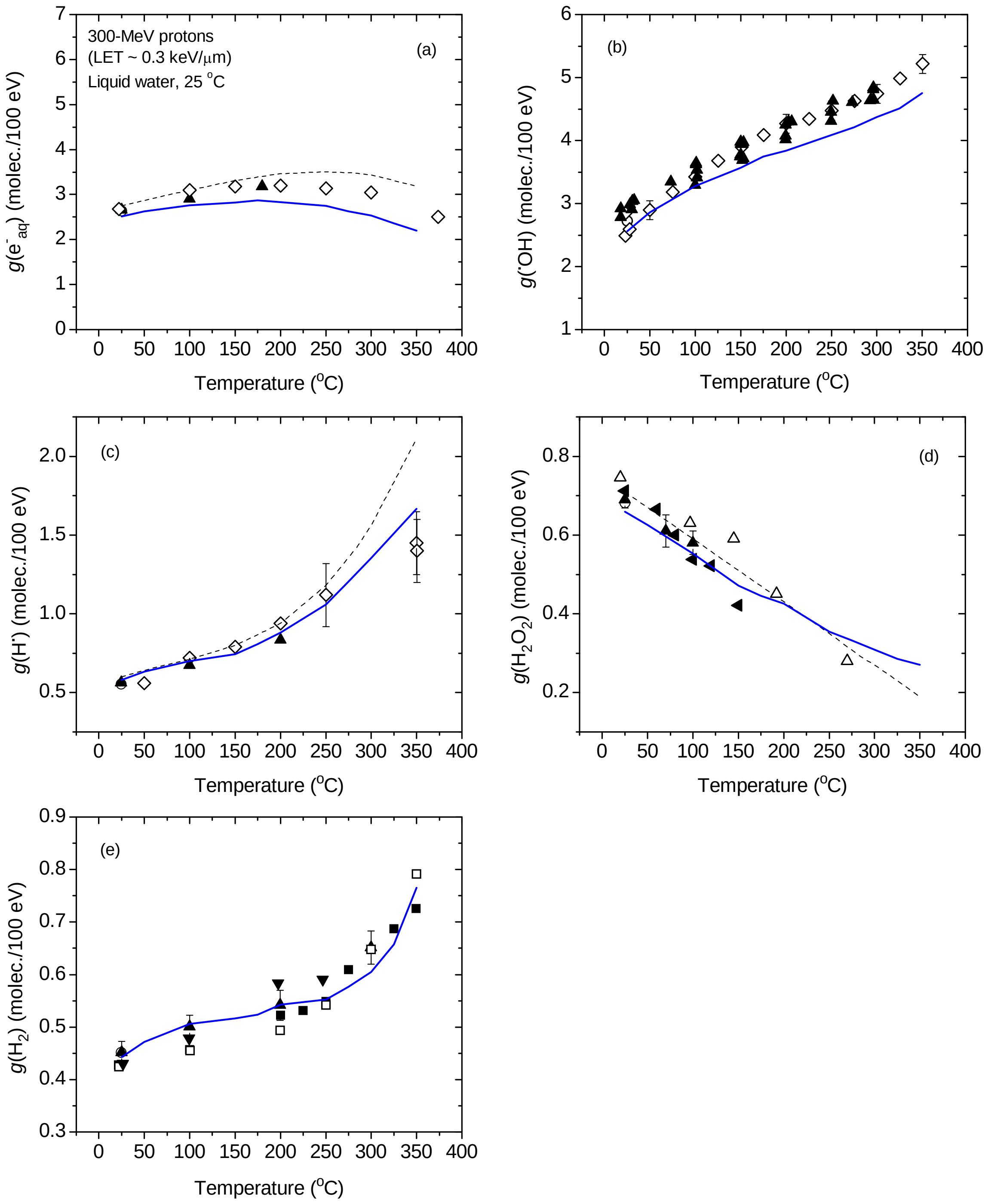

Figure 4: Variation of the primary free-radical and molecular yields (in molec./100 eV) for the radiolysis of liquid water as a function of temperature over the range 25-350°C: (a) $g(e^{-}_{aq})$, (b) $g(^{\bullet}OH)$, (c) $g(H^{\bullet})$, (d) $g(H_2O_2)$, and (e) $g(H_2)$. Simulated results are shown as a solid line. Experimental data are from: [5] (■,□), [8] (□ □ □, recommended temperature dependence for

the *g*-value), [29] (▲), [30] (○), [41] (◄), [42-45] (◊), and [46] (Δ). Note that the *g*-values reported for e^-_{aq} and $^\bullet$OH are slightly elevated (as compared to the true "escape" yields) as a consequence of too high solute scavenging capacities[8] used in the experiments [8,45]. This explains the difference that we observe between our simulated $g(e^-_{aq})$ and $g(^\bullet OH)$ values and the corresponding experimental data, these yields being simply not compared at the same time. Note also that our simulations incorporate the reaction $H^\bullet + H_2O \rightarrow H_2 + {}^\bullet OH$, recently proposed by Swiatla-Wojcik and Buxton [47] to account for the unexplained increase in the yield of H_2 at high temperature. The rate constant used here for this reaction is based on the value of 10^4 M^{-1} s^{-1} at 300°C inferred by Ghandi et al. [48,49] from muon spin spectroscopy experiments.

3.4 Temperature dependence of $g(H_2)$ above 200 °C: on the importance of the reaction $H^\bullet + H_2O \rightarrow H_2 + {}^\bullet OH$

As mentioned above, $g(H_2)$ is observed to continue to increase with temperature, particularly above 200°C [5,29,46]. In an attempt to quantitatively explain this anomalous increase in H_2 yield, an additional channel for H_2 formation was postulated by Swiatla-Wojcik and Buxton (henceforth referred to as SWB) [47,50]. These authors suggested that the reaction of hydrogen atoms with water:

$$H^\bullet + H_2O \rightarrow H_2 + {}^\bullet OH \qquad (1)$$

which can normally be neglected at room temperature, could become important at elevated temperatures. Quite remarkably, Sunaryo et al. [51] already emphasized in 1995 the possible importance of this reaction in the radiolysis of water at high temperatures. Based on a rate constant of 0.086 M^{-1} s^{-1} at 25°C estimated from thermodynamic data, and literature values of $g(H_2)$ as a function of temperature, SWB calculated a corresponding activation energy of ~66.3 kJ/mol over the temperature range 20-300°C. More specifically, they inferred that a reaction rate constant of $\sim 3.2 \times 10^4$ M^{-1} s^{-1} was required to explain the temperature dependence of $g(H_2)$ at 300°C [47]. This value, however, was disputed by Bartels [52] on the basis of thermodynamic arguments. The latter pointed out that this reaction could not be as fast as suggested by SWB and that the correct number for its rate constant was probably an order of magnitude lower. He suggested a value of 2.2×10^3 M^{-1} s^{-1} at 300°C as a best estimate [8,52]. In reply to these comments, Swiatla-Wojcik and Buxton [50] re-analyzed Bartels' thermodynamic estimate and showed, in agreement with his results, that the rate constant of reaction (1) at room temperature was actually three orders of magnitude smaller than originally estimated. However, SWB found 1.75×10^4 M^{-1} s^{-1} for the rate constant at 300°C, thus confirming the high value they had obtained previously.

Without going into all the details regarding the formation of H_2, which have already been discussed at length elsewhere, we show in Fig. 5 the overall variation of $g(H_2)$ as a function of temperature as obtained by our Monte-Carlo simulations. In fact, the calculations are similar to those presented in Fig. 4e, the only difference being the choice of the value of the rate constant assigned to reaction (1). As we can see, using Bartels' rate constant (2.2×10^3 M^{-1} s^{-1} at 300°C) leads to values of $g(H_2)$ that are too low compared with experimental data. Similarly, if we

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[8] The reciprocal of the scavenging capacity gives a measure of the time scale over which the scavenging is occurring.

choose the rate constant given by SWB (3.2×10^4 $M^{-1}s^{-1}$ at 300°C) we obtain too high values of $g(H_2)$.

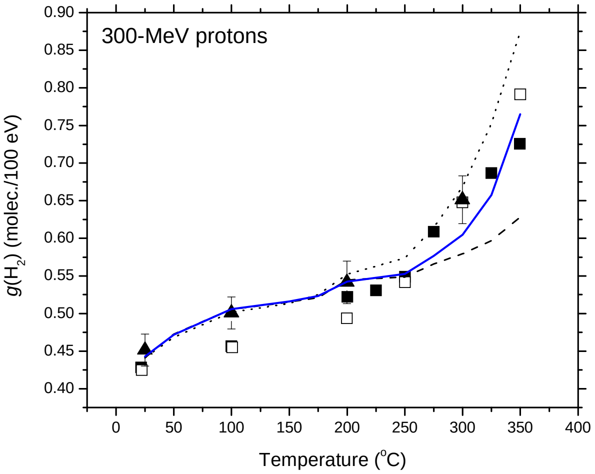

Figure 5: Primary yield of molecular hydrogen versus temperature over the range 25-350°C. Calculated yields are obtained from averages over 150 short (150 μm) track segments of 300-MeV protons (LET ~ 0.3 keV/μm at 25°C) and include the reaction of hydrogen atoms with water. The dotted line shows our simulated results of $g(H_2)$ calculated with the rate constant of reaction (1) given by SWB (3.2×10^4 M^{-1} s^{-1} at 300°C) [47], while the dashed line represents our $g(H_2)$ values computed with the rate constant predicted by Bartels (2.2×10^3 M^{-1} s^{-1} at 300°C) [8,52]. The solid line shows our simulated results of $g(H_2)$ obtained with the value of 10^4 M^{-1} s^{-1} at 300°C inferred by Ghandi et al. [48,49] from muon spin spectroscopy experiments. Experimental data reported here are the same as in Figs. 1 and 4e.

According to our simulations, it clearly appears that reaction (1) is needed to reproduce the unexplained increase in the H_2 yield above 200°C. Moreover, calculations show that the best agreement between simulated and experimental $g(H_2)$ results is obtained with the rate constant recently proposed by Ghandi et al. [48,49] (~10^4 M^{-1} s^{-1} at 300°C).

4. Conclusion

In this work, we re-examined our Monte-Carlo simulation code of the low-LET radiolysis of liquid water at high temperatures in an attempt to reconcile our computed g-values of the various radiolytic products with newly measured or recently re-assessed experimental data over the range from 25 up to 350°C. Using a global-fit procedure, consisting of simultaneously fitting all our computed temperature-dependent g-values to experiment as well as comparing our time-dependent e^-_{aq} yield data to recent picosecond pulse measurements of the decay kinetics of hydrated electrons at different temperatures, we found it necessary – to best reproduce the currently available experimental data, and in particular to take into account the lack of reaction of $e^-_{aq} + e^-_{aq}$ above ~150°C – to introduce a discontinuity around 100-150°C in the temperature dependence of certain parameters that intervene in the physicochemical stage of our code and that are associated with the degree of local structural order of water molecules. The importance of the reaction of hydrogen atoms with water in contributing to the primary yield of H_2 above 200°C was also pointed out.

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