Title

Ab initio spur size calculation in liquid water at room temperature

Authors

Yusa Muroya^{*}, Asokendu Mozumder¹

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

¹ On leave of absence from the Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA.

^{*}Corresponding author. Fax: +81-6-6879-4889. *E-mail address:* muroya@sanken.osaka-u.ac.jp (Yusa Muroya)

Abstract

An attempt was made to calculate the spur size in liquid water at room temperature from fundamental interactions. Electron trapping, elastic scattering, and positive-ion back attraction undergone in sub-excitation and sub-vibrational stages in the 100 fs time scale for thermalization were considered and included in the model. Overall diffusional broadening was estimated to be 41.2 Å, attended by the positive-ion pull back of 24.0 Å, resulting in a calculated spur size of 17.2 Å. Electron trapping is seen in competition with thermalization in the ultimate stage, which results in the trapped electron position distribution as a sum of gaussians.

1. Introduction

In an earlier publication [1], we considered the processes for thermalization of low-energy electrons in liquid water and thereby determined the time scales ($\sim 10^{-13}$ s) for it. Important among these processes are *intramolecular* vibrational and rotational excitation, and dielectric interaction in the sub-excitation stage and *intermolecular* vibrational excitation through H-bond stretching and bending in the sub-vibrational stage. The results so-obtained are now combined with model-computed elastic cross-sections and estimated trapping cross-sections to give the diffusional broadening of trapped electrons in the thermalization time scale. Additionally, we have included the back attraction due to the positive-ion which surprisingly can reduce the diffusional broadening by as much as ~ 50 %.

The size of the electron spur is an important parameter in the calculation of radiation chemical yields in liquid water at room temperature. Along with the distribution of other primary species and the rates and diffusion coefficients of the reactants, this determines the radiation chemical yields that are measured. The spur size (denoted hereinafter as r_s) at elevated temperatures are generally based on that at room temperature [2-5]. The present calculation is done for a single cation-electron pair. Earlier ad hoc adjustments have been done for a given number of ionizations. In almost all earlier calculations of radiation chemical yields in water, using either diffusion or stochastic kinetics or Monte-Carlo simulation, an initial distribution of electrons and other radicals (H, OH etc.) has been assumed which is mostly gaussian [2-5 and references therein]. The r_s is adjusted to give best agreement with a few selected experimental yields. With a reaction scheme, diffusion coefficients and rate constants, calculations are then made for a larger set of yields which are compared with experiments. Adjustments are made until satisfactory agreement is obtained. In this paper we take an ab initio approach, that is we calculate the r_s from basic principles without attempting to adjust with some experimental yields.

In partial modification of our earlier work, we see competition between trapping and thermalization in the final stage. Throughout this paper, we have used experimental data wherever reliable ones are available, supplemented by theoretical estimates when such are not. Contrary to expectation and time-honored usage, we find that the final trapped electron distribution to be a sum of gaussians, rather than a single one, even though moments of all orders are easily calculable. In the next sections we consider sequentially energy loss and time scales involved in sub-excitational and sub-vibrational stages, followed by trapping, diffusional broadening and positive-ion back attraction in all stages. These are then combined to give the entire trapped electron position distribution. In the end we summarize our findings with conclusions.

2. Stages of energy loss and time scales

Following electronic excitation and ionization, which are too fast to be considered for electron thermalization, the stages of electron energy loss and scattering may be enumerated as below: sub-excitation, sub-vibration and trapping, thermalization and post-thermal trapping. In partial modification of our earlier result [6], we are now led to believe that in the later sub-vibrational stage, trapping can compete with thermalization. Further, trapping continues through the post-thermal stage. Our aim is to determine the distribution of trapped electrons which is equivalent to the initial r_s , since detrapping is highly unlikely through the chemical stage [6]. These stages are demarcated by dominant energy loss mechanisms. In the sub-excitation stage, excitation of *intramolecular* vibration is the main mechanism, augmented by dielectric loss [7]. In water at room temperature this stage persists for $\sim 2.89 \times 10^{-13}$ s [1]. In the sub-vibrational stage, excitation of H-bond vibrations, stretching and bending, is the dominant mechanism while rotational excitation makes a minor contribution. In room temperature water, this stage persists for $\sim 0.83 \times 10^{-13}$ s [1]. The thermalization time is the time invested in the two stages which work out to be $\sim 3.72 \times 10^{-13}$ s at room temperature. *Notice that here and elsewhere the times indicated are in the order of magnitude only.*

3. Sub-excitation stage ($\sim 5 - 0.2$ eV)

3.1. Diffusional spread

Lukin [8] has suggested a diffusion length $L_d = (6 D_0 t_0)^{1/2} = 1.6$ to 3.0 nm for photo injected electrons with experimental consistency. Taking $t_0 = 1.1 \times 10^{-13}$ s, one gets $D_0 = 0.39$ to 1.36×10^{-1} cm²/s. Here we take $D_0 = 1.0 \times 10^{-1}$ cm²/s. Corresponding mobility, $\mu = De/k_B T \approx 4$ cm²/Vs, which is not unreasonable. Energy loss rate of sub-excitation electrons, from Fig. 2B of Ref. 1, is 1.95×10^{13} eV/s. Time to reach 0.2 eV from 5 eV is $t_{\text{sub}} = (5.0 - 0.2)/1.95 \times 10^{13} = 2.46 \times 10^{-13}$ s. RMS distance traveled, without positive-ion back attraction (r_{de}) is given by

$$r_{\text{de}} = (6 D_0 t_{\text{sub}})^{1/2} = 38.4 \text{ \AA}. \quad (1)$$

3.2. Positive-ion back attraction

Using Williams' formula [9], with a slight modification to replace $k_B T$ by $2/3$ the value of the mean kinetic energy, i.e.,

$$r_1^3 - r_0^3 = [3e^2 D / \epsilon \langle 2/3 E \rangle] (t_1 - t_0), \quad (2)$$

where subscripts 0 and 1 denote the initial and final positions and where ϵ is the dielectric constant at 10^{-13} s time scale and $\langle E \rangle$ is the appropriate mean electron energy, one can evaluate the positive-ion back attraction with the following data, $r_0 = 0$, $t_0 = 0$, (since slowing down to 5 eV by electronic interactions is a very fast process); $\langle E \rangle = 1.1$ eV and D as given above. *The appropriate dielectric constant is calculated from the modified Cole-Cole equation which fits the*

experimental data at all temperatures. For liquid water it is given by Okada et al [10] in the complex form

$$\varepsilon(\omega) = \varepsilon(\infty) + \frac{[\varepsilon(0) - \varepsilon(\infty)]}{(1 + i\omega\tau)^\beta}, \quad (3)$$

where $\varepsilon(\infty) = 1.77$, $\varepsilon(0) = 78.0$, $\tau = 6.5$ ps and the dispersion index $\beta = 0.936$. We separated the real part of the above equation and evaluated $Re(\varepsilon) \approx 2.142$ in the time scale of 10^{-13} s. Substituting these data in eq. (2), we get the back attraction distance in the sub-excitation stage (r_{pe}) to be 19.1 Å. Comparing with eq. (1), we see that about half of the random scattering is cancelled by positive ion directed back attraction.

4. Sub-vibrational stage and trapping (0.20 - 0.0375 eV)

In this regime, it will be necessary to subdivide the electron energy in several intervals, because of the rapid change of elastic scattering and trapping cross-sections with energy. We consider the following intervals in eV: [0.2, 0.15, 0.10, 0.075, 0.05 and 0.0375]. For elastic scattering, we need to distinguish scattering by molecules constituting traps (pre-existing) and by molecules that are not involved in the trap structure. For the first type, Landau-type resonance scattering gives very large cross-section (~ 600 Å²) at near thermal energies, dwindling down to ~ 6 Å² at 0.2 eV [6,8]. For intermediate energies we have fitted the result with an exponential switching function as follows:

$$\sigma_{tr}^{el}(E) = 2.178 + 1635.92 \exp\left(-\frac{E}{E_{th}}\right). \quad (4)$$

Earlier work of Mozumder [6] rationalized trap density at room temperature to 5.3×10^{20} cm⁻³. Considering 4-6 molecules constituting a trap and a water density of 3.33×10^{22} cm⁻³, the density of trap-bound water molecules works up to $(2.12-3.18) \times 10^{21}$ cm⁻³, leaving the density of trap-free molecules at $(3.12-3.01) \times 10^{22}$ cm⁻³. For these molecules, if we assign a diffusion coefficient 1.0×10^{-1} cm²/s, as before, then the mfp (mean free path) of elastic scattering by these molecules at a full water density would be $L = 6D/v_{eff} = (6 \times 10^{-1}/5 \times 10^7)$ cm = 1.2 Å, where we have used an effective electron velocity $v_{eff} = 5 \times 10^7$ cm/s, representing a typical low-energy electron. For the reduced free water density as computed above, the corresponding mfp would be $1.2 \times 3.3 \times 10^{22} / (3.12 - 3.01) \times 10^{22} = (1.27 - 1.32)$ Å, while we use a mean value of 1.3 Å. At a trap density of 5.3×10^{20} cm⁻³, with $\sigma_{tr}^{el} = 600$ Å² at thermal energy, the mfp for elastic scattering by traps calculates to be $(5.3 \times 10^{20} \text{ cm}^{-3} \times 6.0 \times 10^{-14} \text{ cm}^2)^{-1}$, or 3.14 Å. Considering both types of elastic scatterings, the effective mfp is given by $L_{eff}^{-1} = (1.3)^{-1} + (3.14)^{-1}$, or that $L_{eff} = 0.92$ Å at room temperature thermal energy of 0.0375 eV. Notice that, even though elastic scattering by traps has a very high resonance cross-section, that by non-trap molecules dominate because of their relatively high density.

Mean free paths of elastic scattering by traps at other electron energies are easily calculated with the cross-section of eq. (4) and the same trap density a used before. The results at electron energies of 0.2, 0.15, 0.10, 0.075, 0.05 and 0.0375 eV are respectively 314.0, 67.8, 17.02, 8.60, 4.39 and 3.14 Å.

Elastic scattering mfp by non-trap molecules may be taken with an average value of 1.3 Å over the entire energy span (5.0 - 0.0375 eV), as given in the previous paragraph. Then the effective mfp for all elastic scatterings in the sub-excitation and sub-vibrational energy interval may be computed as $L_{\text{eff}}^{-1} = (L_{\text{tr}}^{\text{el}})^{-1} + (1.3 \text{ Å})^{-1}$. So-computed elastic mfp in the respective energy sub-division varies from 1.3 Å at (5.0-0.2) eV decreasing monotonically to 0.92 Å at 0.0375 eV, as shown in Fig. 1. The effective mfp for elastic scattering perceptively decrease with decrease of electron energy because of the increase of scattering cross-section due to trap-bound molecules.

5. Thermalization time at room temperature

Time to get to 0.2 eV (t_1) has already been computed in the first paragraph under sub-excitation stage to be $t_1 \equiv 2.46 \times 10^{-13}$ s. Energy loss rate in the sub-vibrational regime depends on energy E . It is given by $-dE/dt = k_{\text{eff}} E^{-1/2}$, with $k_{\text{eff}} = 1.584k_s = 4.76 \times 10^{11} (\text{eV})^{3/2} \text{s}^{-1}$ [1]. Here k_s refers to the contribution due to excitation of H-bond stretching only and k_{eff} is that due to excitation of both stretching and bending of H-bonds. On integration, the time needed to come to thermal energy of 0.0375 eV, starting from 0.2 eV is given by (see also the generalized function, eq. (12))

$$t_2 \equiv (2/3) k_{\text{eff}}^{-1} [(0.2)^{3/2} - (0.0375)^{3/2}] = 1.15 \times 10^{-13} \text{ s.} \quad (5)$$

Adding them, the total thermalization time (t_{th}) at room temperature is computed to be

$$t_{\text{th}} = t_1 + t_2 = 3.61 \times 10^{-13} \text{ s.} \quad (6)$$

6. Trapping in pre- and post-thermal stages

Rate of trapping at energy E is given by

$$k(E) = n_t \sigma_t(E) v(E) \text{ s}^{-1}, \quad (7)$$

where $v(E)$ is electron velocity at energy E and n_t , σ_t respectively are trap density (constant) and trapping cross-section at energy E . At thermal energy (0.0375 eV), trapping cross-section has been rationalized to be 20 Å^2 [6]. At other energies it may be assumed to be inversely proportional to velocity, that is, directly to the transit time across the trap. Thus, at energy E ,

$\sigma_t(E)/\sigma_{th} = (0.0375/E)^{1/2}$. With the above stipulation of thermal trapping cross-section of $20 \text{ \AA}^2$, Fig. 2 gives the cross-section at other electron energies, noting as in Ref. 6, that the trapping cross-section is zero for $E > 0.2 \text{ eV}$. It is seen that the trapping cross-section increases with the decrease of electron energy.

To the approximation used here, the rate of trapping remains constant (see the above equation for $k(E)$) at a value $1.24 \times 10^{13} \text{ s}^{-1}$. Considering that the electron remains untrapped till it reaches the energy 0.2 eV , the probability that the electron will remain untrapped at a lower energy would be given by

$$P(E) = \exp[-1.24 \times 10^{13} \times (0.2 - E) / (dE/dt)_{sub}], \quad (8)$$

where $(dE/dt)_{sub}$ indicates the rate of energy loss of sub-vibrational electrons. This equation derives from the relation, $-dP(E)/dt = kP(E)$, with the solution $P(E) = A \exp(-kt)$, being the constant of integration. Considering that the electron remains untrapped at energy 0.2 eV , and eliminating t in the sub-vibrational regime by writing $E = 0.2 - (dE/dt)_{sub} \cdot t$, where $(dE/dt)_{sub}$ is considered constant, the above equation for $P(E)$ is easily derived satisfying the boundary condition $P(E) = 1$ at $E = 0.2 \text{ eV}$. The rate of energy loss, $(dE/dt)_{sub}$, actually depends on energy, but for the present purpose we take an average value $0.91 \times 10^{12} \text{ eVs}^{-1}$ [1]. Substituting in the above equation, we get $P(E) = \exp[-13.6 \times (0.2 - E)]$. The probability, so calculated, for the electron to remain untrapped at a given energy is shown in Fig. 3. Note that at thermalization, there are some untrapped electrons. Therefore, prior to thermalization, there is a competition between thermalization and trapping. Mean trapping time of post-thermal electrons, of the remaining probability of 0.11, is

$$\langle t_r \rangle_{post-th} = k^{-1} = (1.24 \times 10^{13})^{-1} = 0.81 \times 10^{-13} \text{ s}. \quad (9)$$

7. Diffusional spread by elastic scattering in the sub-vibrational regime

Let the elapsed time between energies E_1 and E_2 be Δt . Between these energies, the diffusion coefficient is

$$D = (1/6)L_{eff} \cdot v = (1/6)L_{eff}(2E/m)^{1/2}, \quad (10)$$

where E may be taken as $(E_1 E_2)^{1/2}$. In the i -th interval, the diffusional spread would be

$$\sigma_i^2 = 6D\Delta t_i = L_{eff}(2E/m)^{1/2}\Delta t_i. \quad (11)$$

The mean free paths are taken from Fig. 1. The elapsed time in each interval, between energies E_2 and E_1 , is computed by a generalization of eq. (5), that is

$$\Delta t = (2/3) k_{eff}^{-1} (E_2^{3/2} - E_1^{3/2}), \quad (12)$$

Where energies are in eV and time in s. Using these data, following Table 1 is generated for diffusional spread in respective energy intervals.

The trapping probabilities in the respective energy intervals are obtained from Fig. 3 as the *difference* between successive energy values. For example, between energies 0.2 and 0.15 eV, the trapping probability is $p_1 = 0.493$; similarly, $p_2 = 0.250$, $p_3 = 0.074$, $p_4 = 0.053$ and $p_5 = 0.020$ in downward energy intervals. The diffusional spread of pre-thermal trapped electrons are now obtained by weighing the last column of Table 1 with these respective probabilities, obtaining thereby a total of

$$\sigma_{\text{th}}^2 = \sum_{i=1}^5 p_i \sigma_i^2 = 147.5 \text{ \AA}^2. \quad (13)$$

To get the total spread of trapped electrons we must add the contribution of post-thermal trapping. Post-thermal diffusion coefficient is $0.03 \text{ cm}^2/\text{s}$ (see Table 1). With a mean trapping time $0.81 \times 10^{-13} \text{ s}$, from eq. (9), the contribution of post-thermal spread of trapped electrons is computed to be

$$\sigma_{\text{post-th}}^2 = 6D\langle t_r \rangle_{\text{post-th}} = 145.9 \text{ \AA}^2. \quad (14)$$

Combining this with eq. (13) and with their respective probabilities $\left(\sum_{i=1}^5 p_i = 1 - p_6 \right)$ and p_6 , we get the sub-vibrational spread for trapping (pre- and post-thermal) as

$$\sigma^2 = (1.0 - p_6) \sigma_{\text{th}}^2 + p_6 \sigma_{\text{post-th}}^2 = 147.4 \text{ \AA}^2. \quad (15)$$

For this part, the rms diffusional spread $r_{\text{dv}} = (3/2)^{1/2} \sigma = 14.9 \text{ \AA}$. This is now combined with the sub-excitation diffusional spread of rms value r_{de} ($38.4 \text{ \AA}$, see eq. (1)). Then the total diffusional rms spread (r_{dtot}) for trapping and thermalization between 5.0 and 0.0375 eV would be given by

$$r_{\text{dtot}} = (r_{\text{de}}^2 + r_{\text{dv}}^2)^{1/2} = 41.2 \text{ \AA}. \quad (16)$$

So far, we have not considered the positive-ion back attraction in the sub-vibrational stage, which will be considered next.

8. Positive-ion back attraction:

Williams' formula [9] gives, for each sub-division in the sub-vibrational stage (see eq. (2)):

$$r_i^3 - r_{i+1}^3 = 9(e^2/2)D_i \Delta t_i / \varepsilon_i E_i = (3e^2/4)\sigma_i^2 / \varepsilon_i E_i, \quad (17)$$

where e is electronic charge and the left hand side shows the positive-ion back attraction in the $i+1$ interval. The other symbols have their usual significance. The extreme rhs of the equation is obtained by using $\sigma_i^2 = 6D_i\Delta t_i$. To each of these expressions, appropriate sub-divisional probabilities should be attached. Using the data as before, Table 2 is generated for the weighted contribution to the positive-ion back attraction in each sub-division of energy. Sum of the extreme right hand side multiplied by $(3/4)$ gives $6690.5 \text{ \AA}^3$. Therefore, positive-ion back attraction in the sub-vibrational stage (r_{pv}) is calculated to be $(6690.5)^{1/3} = 18.8 \text{ \AA}$. Combining this with the positive-ion back attraction in the sub-excitation stage, r_1 (see the section 3.2), we get the total back attraction (r_{ptot}) as $r_{ptot} = (r_{pe}^3 + r_{pv}^3)^{1/3} = 24.0 \text{ \AA}$. Notice that comparable contribution to back attraction comes from sub-excitation and sub-vibration stages, with energy intervals as defined in Table 1. On this basis, we define the r_s at room temperature in liquid water as $r_s = r_{dtot} - r_{ptot} = 17.2 \text{ \AA}$ (rms).

9. Entire trapped electron position distribution

In the sub-vibrational stage, the spatial distribution of the trapped electron is given by

$$f(\rho) = \pi^{-3/2} \sum_i p_i \sigma_i^{-3/2} \exp\left(-\frac{\rho^2}{\sigma_i^2}\right), \quad (18)$$

where, in the above equation, $\rho = r$ minus positive-ion back attraction in each sub-division of energy, which can be computed in the same way as in Table 2. Their actual values are not germane to the discussion that follows. The probabilities p_i of trapping in each sub-division of energy are found in the same table. Note that the distribution given in eq. (18) is a genuine probability since $f(\rho) > 0$ (*all* ρ) and $\int_0^\infty 4\pi\rho^2 f(\rho) d\rho = 1$, and that the gaussians and the probability factors are separately normalized. **However, $f(\rho)$ is generally not gaussian, but a combination of several such distributions**, even though the mean and the mean square are clearly given by $\sum_i \langle \rho_i p_i \rangle$ and $\sum_i \langle \rho_i^2 p_i \rangle$ respectively and similarly for other moments.

10. Summary and conclusion

The spur size, r_s , in liquid water at room temperature was estimated from fundamental interactions. We found the diffusional spread of sub-excitation electrons (r_{de}) to be $38.4 \text{ \AA}$ (rms), however mitigated by the positive-ion back attraction, r_{de} of $19.1 \text{ \AA}$. In the sub-vibrational regime, elastic scattering by both trap and non-trap molecules give a diffusional spread (r_{dv}) of $14.9 \text{ \AA}$ (rms) while the positive-ion pull back (r_{pv}) is estimated at $18.8 \text{ \AA}$. Overall diffusional broadening (r_{dtot}) is $41.2 \text{ \AA}$ (rms), attended by the positive-ion pull back (r_{ptot}) of $24.0 \text{ \AA}$, resulting in a so-defined r_s of $17.2 \text{ \AA}$ (rms).

To our knowledge, this is the first attempt to calculate the r_s in water from fundamental interactions involving random elastic scattering, positive-ion back pull and trapping (in both pre- and post-thermal regimes). All earlier spur sizes, used in diffusion or stochastic kinetics, were initially adjusted to a selected group of experiments [2-5, and references therein]. Schwarz [2] did the first systematic diffusion kinetic calculation in room temperature liquid water and obtained a hydrated electron Gaussian distribution with an average distance of 23 Å from the spur center, by best adjustment with a few cardinal experiments, while the mean OH distance was 7.5 Å. All later calculations have essentially followed these values with minor variations. We cannot directly compare these numbers with our finding, because our trapped electron distribution is not a single Gaussian, but a combination several such distributions (see section 9). However, it is worth noting that Schwarz's Gaussian distribution gives an rms value of 25.0 Å for the hydrated electron, while we compute 21.2 Å, both using Gaussian functions. In the present work, a significant competition is seen between thermalization and trapping toward the end of the sub-vibrational regime.

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Fig. 1. The elastic scattering mfp by traps (L_{tr}^{el}), that by trap-free molecules (L_{nontr}^{el}), and the effective mfp (L_{eff}) calculated from L_{tr}^{el} and L_{nontr}^{el} . Note that the red-dot line represents L_{nontr}^{el} which is constant (1.5×10^{-10} m) over the whole energy range from 0.0375 to 5 eV (sub-excitation- as well as sub-vibrational- level). Please also note that L_{eff} in between 0.2 to 5 eV almost corresponds to L_{nontr}^{el} (1.5×10^{-10} m)(see the eqs. in the text).

Fig. 2. Energy dependence of the trapping cross-section calculated for sub-vibrational electron (below 0.2 eV).

Fig. 3. Energy dependence of the probability for the sub-vibrational electron to remain untrapped ($P(E)$). Note that the differences represented as p_1 to p_5 correspond to the trapping probabilities of the pre-thermal electrons in the respective energy intervals illustrated in Table.1.

Table 1

Parameters of diffusional spread by elastic scattering in the sub-vibrational energy intervals

i	Energy interval	$\langle E \rangle^a$ (eV)	L_{eff} (Å)	D (cm ² /s)	Δt (10 ⁻¹³ s)	σ_i^2 (Å ²)
1	0.20-0.15	0.17	1.3	0.08	0.44	213.0
2	0.15-0.10	0.12	1.3	0.067	0.37	148.0
3	0.10-0.075	0.087	1.2	0.052	0.16	46.0
4	0.075-0.05	0.061	1.1	0.040	0.13	32.0
5	0.05-0.0375	0.043	1.0	0.030	0.055	9.9

^a Geometric mean. Note that in this table and in what follows later σ is the spread of electron position distribution and not a cross-section.

Table 2

Parameters of weighted contribution to the positive-ion back attraction in each sub-division (*i*) of energy

<i>i</i>	<i>E</i> (eV)	<i>p_i</i>	σ_i^2 (Å ²)	ε	$\sigma_i^2 / \varepsilon E$ (= α)	$pe^2\alpha$ (Å ³)
1	0.17	0.493	213.0	2.142	576.0	4091
2	0.12	0.250	148.0	2.142	567.0	2039
3	0.087	0.074	46.0	2.142	247.0	263
4	0.061	0.053	32.0	2.142	242.0	184
5	0.043	0.020	9.9	2.142	107.0	31
6 ^a	0.038	0.110	146.0	2.657	1464.0	2313

^a Post-thermal stage

Figure 1

Figure 2

Figure 3