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Research paper

Ab initio spur size calculation in liquid water at room temperature

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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

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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 (~5–0.2 eV)

3.1. Diffusional spread

Lukin [8] has suggested a diffusion length $L_d = (6D_0t_0)^{1/2} = 1.6$–3.0 nm for photo injected electrons with experimental consistency. Taking $t_0 = 1.1 \times 10^{-13}$ s, one gets $D_0 = 0.39$–1.36×10^{-1} cm^2/s. Here we take $D_0 = 1.0 \times 10^{-1}$ cm^2/s. Corresponding mobility, $\mu = De/k_BT \approx 4$ cm^2/V s, 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 $t_{sub} = 2.46 \times 10^{-13}$ s. RMS distance traveled, without positive-ion back attraction (r_{de}) is given by

$$r_{de} = (6D_0t_{sub})^{1/2} = 38.4 \text{ Å}. \quad (1)$$

3.2. Positive-ion back attraction

Using Williams' formula [9], with a modification to replace k_BT by 2/3 the value of the mean kinetic energy, i.e.,

$$r_1^3 - r_0^3 = \left[\frac{3e^2D}{\varepsilon\langle 2/3E\rangle}\right](t_1 - t_0), \quad (2)$$

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, as shown in the appendix, 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 Å^2) at near thermal energies, dwindling down to ~6 Å^2 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} cm^2/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 $\sigma_{tr}^{el} = 600$ Å^2 at thermal energy, the mfp for elastic scattering by traps calculates to be $(5.3 \times 10^{20}$ cm$^{-3} \times 6.0 \times 10^{-14}$ 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 $L_{eff}^{-1} = (L_{tr}^{el})^{-1} + (1.3\text{ A})^{-1}$. 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 $-dE/dt = k_{eff}E^{-1/2}$, with $k_{eff} = 1.584k_s = 4.76 \times 10^{11}$ (eV)$^{3/2}$ 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))

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

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

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