Processes and time-scales of energy loss of low-energy electrons (<5 eV) in liquid water

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ARTICLE INFO

Article history:

Received 13 August 2014

In final form 16 October 2014

Available online 23 October 2014

ABSTRACT

The various processes responsible for the energy degradation and eventual thermalization of low-energy subexcitation electrons (<5 eV) in liquid water are completely delineated for the first time, while previous work assumed the formation of thermalized electrons in the 10^{-11} – 10^{-12} s for liquid water at room temperature. Chief among these are *intramolecular* vibrational and rotational excitation, dielectric interaction and excitation of *intermolecular* vibration through H-bond stretching and bending. Cross-sections for these processes are taken from experiments or derived theoretically. Individual time scales are obtained for subexcitational and subvibrational regimes in water at room and higher temperature.

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1. Introduction

It is well-known that as the electron loses energy, the mechanism of energy loss changes gradually. At first, it is by ionization and electronic excitation. The electron becomes subexcitational when its energy falls below the first excitation potential [1], which in liquid water is ~ 5 eV. Such electrons lose energy by exciting *intramolecular* vibration and rotation, and also by dipolar interaction in polar liquids [2]. Eventually, the electron energy falls below the molecular vibrational level which it cannot excite effectively, but it is still very hot. Such electrons, called subvibrational, play an important role in thermalization as seen in the analysis of free-ion yield in liquid hydrocarbons [3,4]. Taking a cue from Raman scattering process in the liquid, electron-induced cross-section was linked with a thermalization distance distribution, and the result was compared with experiment on the free-ion yield. Whereas in the case of liquid hydrocarbons, the relevant cross-sections (elastic and inelastic) were adjusted for the experimental free-ion yield at room temperature, here we calculate the cross-sections in liquid water from first principles. In this sense, this is the first attempt to thermalization. Several avenues of energy loss that are available in the condensed phase [2,5–7] are considered at room and higher temperature.

In the next section, we will provide a theoretical background of the various loss processes. This will be followed by results obtained and discussion. Finally, we conclude with a summary.

2. Background of energy loss of low-energy electrons

Theoretical, first principle, calculation for the excitation of *intramolecular* vibration by subexcitation electrons is not reliable in any phase. However, Michaud and Sanche [5] have developed a technique, called ‘two stream multiple-scattering analysis’, using which they have evaluated the relevant cross-sections per scatterer by analyzing high-resolution electron energy loss experiments (HREEL). In these experiments, they measure the back scattered electron intensity from layers of condensed water at 14 K as functions of energy loss and angle between 14° and 45° . They then fit the cross-sections for various elastic and inelastic processes to get close agreement between experiment and computation. The incident electron energy is varied in the interval 1–18 eV. In this sense the cross-sections obtained by Michaud and Sanche are a combination of theory and experiment. For our purpose, we use the cross-sections for the two stretching vibrations, symmetric and asymmetric ν_1 and ν_3 , respectively at 0.453 and 0.466 eV and that for the bending vibration at 0.198 eV. As these energies are not expected to vary with density or phase, we think it is reasonable to use these for liquid water. With known density of scatterers, the quanta of energy loss, electron velocity and the cross-section, the rate of energy loss at electron energy W is easily computed at any temperature, by density scaling. On the other hand, certain other processes, such as cross-sections for rotational excitation, *intermolecular* vibrational excitation, elastic scattering etc., cannot be

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obtained for liquid water, from the experiments of Michaud and Sanche, because the probabilities of these processes vary with density and cannot be density scaled. In particular, rotational excitation is frequently mixed with elastic scattering and in the liquid phase, often hindered. Here we use experimental data for the absorption coefficient in the (8–80) cm⁻¹ interval [7] and convert it to electron-induced cross-section (vide infra). Rotational excitation energy may be obtained from Kimura et al. [8].

Fröhlich and Platzman [2] pointed out a separate mechanism of energy loss of subexcitation electrons in polar media, i.e., by the interaction of the electric field of the electron on the permanent dipoles of the medium. Following a method originally owing to Fermi, they obtained, with some reasonable approximation, the following expression for the rate of energy loss:

$$-\left(\frac{dE}{dt}\right)_d = \left(\frac{\pi e^2}{a}\right) \left[\frac{\varepsilon_s - \varepsilon_{ir}}{\tau \zeta^4}\right]. \quad (1)$$

In Eq. (1), E is the electron energy at time t , e is the electronic charge, a is an intermolecular distance parameter, ε_s , respectively ε_{ir} are the static and infra-red dielectric constants, τ is the dielectric relaxation time, ζ is the refractive index and the subscript d is used to indicate that the electron energy loss is due to dielectric interaction only. With reasonable values of the physical parameters for liquid water at 20 °C, Fröhlich and Platzman argue that nearly equal contribution to the rate of energy loss of subexcitation electrons originates from intramolecular vibrational excitation and by dielectric interaction, both being $\sim 10^{13}$ eV/s. At present, dielectric data for liquid water are available over a wide interval of temperature [9]. Refractive index [10] and molecular density of water [11] can be obtained from standard references.

Subvibrational interactions that ultimately thermalize the electron have been described in liquid *n*-hexane, assuming intermolecular vibration of a quantum ~ 0.01 eV [3,4]. Qualitatively the idea was borrowed from that part of the Raman spectrum in the liquid for which there is no correspondence in the gas phase. Probability of this process was adjusted to the free-ion yield at room temperature, and then the theory was extended to other temperatures and for an applied external field. In the present case of liquid water, we reverse the procedure and estimate the cross-sections from available infra-red experiments and a theory adapted for this process. Later, these cross-sections will be combined with estimated cross-section for elastic scattering and trapping to generate a thermalization distribution to compare with radiation chemical experiments at room and higher temperatures [12].

Far-IR Raman spectra in liquid water were recorded almost immediately after the discovery of the Raman effect [13,14]. These consist of two broad features at ~ 170 and ~ 60 cm⁻¹ and any number of weaker bands. The original interpretation of these bands in terms of intermolecular motion has been substantiated by later studies [15]. Accordingly, these have been assigned respectively to H-bond stretching and bending, also designated as restricted translation of water molecules along and perpendicular to the H-bond. More recent theoretical analysis indicates that the 60 cm⁻¹ band is strongly localized while that at ~ 180 cm⁻¹ is not strongly localized, but related by H-bond connectivity [6]. It is the purpose of the present work to relate the energy loss of subvibrational electrons in liquid water to H-bond stretching and bending motions.

Since optical absorption is related to transitions induced in the medium by a charged particle through its electric field, it should be possible to derive the cross-section for energy loss of a subvibrational electron in terms of far-IR absorption data in the liquid [7].

Within the Born approximation, the differential cross-section for energy loss ξ of an electron of energy E is given by [16]

$$\frac{d\sigma}{d\xi} = \kappa \left[\frac{f'(\xi)}{\xi} \right] \ln \left(\frac{\xi_m}{\xi} \right), \quad (2)$$

where in Eq. (2), the kinematic factor $\kappa = \pi e^4/E$, with e as the electronic charge, $f'(\xi)$, the differential oscillator strength for the energy loss for a maximum of ξ_m . At first sight, it may seem inappropriate to use the Born approximation for low-energy electrons. However, the transit time of a subvibrational electron over an H-bond is $\sim 10^{-15}$ s, much shorter than the infra-red vibrational period in liquid water $\sim 2 \times 10^{-13}$ s. Therefore, the electric field due to the electron acts as an impact over the H-bond, and the application of Born approximation can be justified for low-energy electrons for very low energy loss.

Now, the molar extinction coefficient ε [mol⁻¹ l cm⁻¹] is related to the differential oscillator strength by $f' = 4.32 \times 10^{-9} \varepsilon$, where f' is now expressed as per unit wave number ν . Further, experimental absorption data are usually expressed in terms of the absorption coefficient α (cm⁻¹) [7] for which we have $\alpha = 2.303 \varepsilon \eta$, where η is the absorber density in moles/liter; the factor 2.303 appears in this equation because α uses natural logarithm whereas ε is defined as log₁₀. Combining these factors, we get

$$\frac{d\sigma}{d\xi} = 4.32 \times 10^{-9} \left[\frac{\kappa}{\xi} \right] \left[\frac{\varepsilon(\nu)}{hc} \right] \ln \left(\frac{\xi_m}{\xi} \right), \quad (3)$$

where we have used the identity $d\nu/d\xi = (hc)^{-1}$, h being the Planck's constant and c , the velocity of light. Evaluating $hc = 1.238 \times 10^{-4}$ eV cm, we now derive the working formula given in Eq. (4).

$$\frac{d\sigma}{d\xi} \text{ (Å}^2\text{/eV)} = \left[\frac{9.86 \times 10^{-3}}{E(\text{eV})\xi(\text{eV})} \right] \left(\frac{\alpha}{\eta} \right) \ln \left(\frac{\xi_m}{\xi} \right) \quad (4)$$

With the above-derived cross-section, one can compute the rate of energy loss of the electron for a particular subvibrational process (stretching or bending) from which the time scale of degradation down to the thermal energy ($3k_B T/2$) is easily obtained.

3. Results and discussion

For the purpose of the present letter, it would be convenient to divide the energy loss of low-energy electrons in water into two stages. Stage A extends from ~ 5.0 to ~ 0.5 eV, where the electron energy is subexcitation [1], but above the subvibrational limit. Stage B covers the interval ~ 0.5 eV to thermal energy, noting that the end point is temperature dependent.

In stage A there are two competing processes for energy loss: excitation of *intramolecular* vibration [5] and dielectric interaction [2]. Fröhlich and Platzman's expression (Eq. (1)) for dielectric energy loss depends on temperature through dielectric data and refractive index, but it is independent of electron energy. Rate of energy loss for intramolecular vibrational excitation is obtained directly from experimental data [5] using the formula $-(dE/dt)_{\text{intra}} = \rho \nu \sum_i h \nu_i \sigma_i$, where ν is the electron velocity at energy E , ρ is the water density, and σ_i is the cross-section for exciting a mode of vibration of energy $h \nu_i$. Of the two stretching frequencies, experiment does not distinguish between their energies at 0.453 and 0.466 eV, but the bending energy is clearly distinguished at ~ 0.2 eV. Water density at different temperatures has been kindly supplied by D. Swiatla-Wojcik [17], which is converted to number density of molecules. Figure 1 shows the rate of energy loss of subexcitation electrons in stage A due to intramolecular vibrational excitation as a function of electron energy at two temperatures (300 and 623 K). This rate decreases with temperature

Figure 1. Energy loss rate of subexcitation electrons vs. electron energy at two temperatures.

due to lowering of density. At the same temperature it increases with electron energy mainly due to the cross-section of stretching vibrations. Subexcitation electrons have a nearly universal energy distribution as argued by Platzman [1]. Here we use a modified version given by Elkomoss and Magee [18], shown in Eq. (5).

$$f(\varepsilon) = \frac{[1 + E_0/I]^2}{E_0[1 + E_0/2I]} \cdot \left[1 + \frac{\varepsilon}{I}\right]^{-3} \quad (5)$$

In Eq. (5), ε is the electron energy and E_0 and I are respectively the first excitation and ionization potentials. The average subexcitation energy, from Eq. (5), is given by $\langle\varepsilon\rangle = (E_0/2)(1 + E_0/2I)^{-1}$, which for water is ~ 2.06 eV at $E_0 = 5$ eV and $I = 11.7$ eV [16]. Subsequent calculations are done with this average energy.

For the energy loss rate due to dipolar interaction at higher temperatures, we have normalized its value relative to that at 25 °C for which we take the estimated value of 1.0×10^{13} eV/s [2]. We thus get

$$\frac{-(dE/dt)_d(T)}{-(dE/dt)_d(25^\circ\text{C})} = \left(\frac{\rho_T}{\rho_{25}}\right)^{1/3} \frac{(\varepsilon_s - \varepsilon_{ir})_T}{(\varepsilon_s - \varepsilon_{ir})_{25}} \left(\frac{\tau_{25}}{\tau_T}\right) \left(\frac{\zeta_{25}}{\zeta_T}\right)^4, \quad (6)$$

where, in Eq. (6), we have used $a \propto \rho^{-1/3}$. Dielectric data at different temperatures have been taken from Refs. [9,19]. The so-obtained dielectric relaxation time and energy loss rate due to dielectric interaction is shown in Figure 2A as functions of temperature. Figure 2B shows the total energy loss rate of subexcitation electrons in stage A, as the sum of intramolecular vibrational interaction and that due to dielectric interaction, as a function of temperature. Notice that this rate generally decreases with temperature except for a shoulder near the critical temperature.

Walrafen et al. [15], among others, have investigated low-frequency Raman spectra over 0–350 cm^{-1} . These show important intermolecular vibrations at ~ 170 and 60 cm^{-1} , in close agreement with absorption experiments [7]. Actual experiments have been performed from 10 to 70 °C, but the results can be extrapolated to higher temperatures. These so-determined absorption coefficients have been used in Eq. (4) to obtain electron-induced cross-section for intermolecular vibrational excitation cross-section. Of the various far-IR experiments performed in liquid water [7,20–22], we have used the data of Ref. [7], as being most appropriate for the present purpose, because of the clarity of presentation. The authors have used Fourier Transform Infrared Spectrometry with synchrotron radiation as the source. The very low-frequency

Figure 2. (A) Dielectric relaxation time relative to that at 298 K and dielectric energy loss rate vs. T . (B) Average energy loss rate (intramolecular vibration + dielectric) in the subexcitation regime vs. T .

absorption, attributable to H-bond bending vibration, is not observed in ice. It is specific to the liquid phase. Its peak frequency does not change appreciably with temperature. On the other hand, the peak frequency of the H-bond stretching mode decreases almost linearly with temperature, which has been fitted by the authors to the equation $f_{\text{peak}} (\text{cm}^{-1}) = -0.293T (\text{K}) + 260$.

We have extrapolated this equation up to 623 K where equation $f_{\text{peak}} = 77.5 \text{ cm}^{-1}$, which seems to us as reasonable. For energy degradation of subvibrational electrons, it is the S (stretching) band that is more significant, although the B (bending) band contribution is not negligible, especially at high temperatures. By a fitting procedure, the S-band absorption has been described to be Gaussian, with characteristic frequency ω_s (identified here with f_{peak}) and standard deviation σ_s . The Gaussian function dwindles to insignificance when the argument is ~ 4 , implying that ξ_m in Eq. (4) can be taken as $\xi_m = 2\sqrt{2}\sigma_s + f_{\text{peak}}$. However, the B-band absorption is assigned to a damped harmonic oscillation with characteristic frequency ω_B and damping constant γ_B which are determined by a similar procedure. The integrated absorption over frequency shows little dependence on temperature for both bands. This implies that the standard deviation of the stretching mode decreases with temperature while the damping of the bending increases. These values are used in Eq. (4) for the computation of cross-sections of energy loss of subvibrational electrons. The integrated cross-section thus automatically incorporates the respective ξ_m for the two bands.

Table 1
Density of water molecules and of H-bonded molecules [17].

T (K)	298	373	473	573	623	653
ρ	0.998	0.97	0.88	0.74	0.61	0.45
$\langle H \rangle$	3.34	2.78	2.26	1.76	1.44	1.07
n	91.68	74.17	54.70	35.82	24.16	13.24

For numerical calculation, it is convenient to rewrite the integrated cross-section as follows:

$$\sigma(\text{\AA}^2) = \left[\frac{9.86 \times 10^{-3}}{E(\text{eV})n} \right] \left[x_{\max} \int_{x_{\min}}^{x_{\max}} \alpha(x) dx - \int_{x_{\min}}^{x_{\max}} x \alpha(x) dx \right], (7)$$

where, in the above equation, the independent variable has been changed to $x = \ln \xi$, n denoting the H-bond density in moles/liter. While the H-bond density for stretching vibration equals one-half the density of bonded molecules that for the bending motion has to be doubled because of two possible perpendicular vibrations for each H-bond. The density of bonded molecules in water as a function of temperature has been kindly supplied by D. Swiatla-Wojcik [17] and shown in Table 1, as a function of T .

In this table, ρ is the density of water in g/ml and $\langle H \rangle$ denotes the average number of H-bonds per water molecule; n is the density of H-bonds in moles per liter (one H-bond per two bonded molecules).

This and the ordinary density of water are also displayed in Figure 3 which incorporates some data for the supercritical fluid. The integrals in Eq. (7) are the average values of the absorption coefficient α and its first moment $x\alpha$, so that the working formula may be displayed as follows:

$$\sigma(\text{\AA}^2) = \left[\frac{9.86 \times 10^{-3}}{E(\text{eV})n} \right] (x_{\max} - x_{\min}) [x_{\max} \langle \alpha \rangle - \langle x\alpha \rangle] (8)$$

In Eq. (7) $x_{\max} = \ln \xi_m$ and $x_{\min} = \ln \xi_{\min}$. As an example of a typical calculation consider a subvibrational electron of energy 0.3 eV interacting with H-bond stretching vibration at room temperature (RT). Using $n = 91.68$ from Table 1, $x_{\max} = 5.598$, $x_{\min} = 4.33$ and estimating $\langle \alpha \rangle = 500$ and $\langle x\alpha \rangle = 2500$ from Ref. [7], we get $\sigma = 0.136 \text{\AA}^2$ for that process. For the excitation of H-bond bending vibration by the same electron we take $n = 2 \times 91.68$ and estimate $x_{\max} = 4.3820$, $x_{\min} = 2.0794$, $\langle \alpha \rangle = 375$ and $\langle x\alpha \rangle = 1355$ [7], resulting in $\sigma = 0.119 \text{\AA}^2$ for that kind of excitation. Similar computations have been made over the entire energy interval of subvibrational electrons and over a range of higher temperatures using appropriate data.

We have remarked in the previous paragraph that the integrated cross-sections have little dependence on T . Therefore, those

Figure 3. Density of water molecules and H-bonds vs. T . SCF, supercritical fluid. **Figure 4.** Energy loss rates in the subvibrational regime due to stretching and bending of H-bonds as functions of electron energy at two temperatures.

for intermolecular vibrational excitation cross-section depend on temperature only through the density of H-bonds. These are approximately inversely proportional to electron energy (cf. Eq. (7)). This gives the energy loss rate of subvibrational electrons as

$$-\frac{dE}{dt} = \sigma v n \xi', (9)$$

where σ is the integrated cross-section, v is the electron speed at energy E , n is the effective H-bond density and ξ' is a typical far-IR energy in the respective band (0.0225 eV at 180 cm^{-1} band and 0.0075 eV at 60 cm^{-1} band). For the cross-section we use Eq. (8) for the stretching or bending vibration as the case may be. Note that $\sigma v n$ represents the collision frequency and $v (\text{cm/s}) = 5.93 \times 10^7 E (\text{eV})^{1/2}$. Since $\sigma \propto E^{-1}$ and $v \propto E^{1/2}$, one gets from Eq. (9),

$$-\frac{dE}{dt} = \kappa_S E^{-1/2}, (10)$$

where κ_S , for the stretching vibration, is a constant at a given T . In the example cited in the previous paragraph, $\sigma = 0.136 \text{\AA}^2$ for stretching at RT which results in a collision frequency of $2.443 \times 10^{13} \text{ s}^{-1}$ for an electron of energy 0.3 eV. Thus, we get from Eq. (9), the rate of energy loss $5.5 \times 10^{11} \text{ eV s}^{-1}$, which on comparison with Eq. (10) gives $\kappa_S = 3.013 \times 10^{11} (\text{eV})^{3/2} \text{ s}^{-1}$ at RT. Similar calculation for the bending vibration gives $\kappa_B = 1.758 \times 10^{11} (\text{eV})^{3/2} \text{ s}^{-1}$ at RT. For both kinds of intermolecular vibrational excitation, the rate of energy loss and therefore $\kappa_{S,B}$ depend on temperature only upon H-bond density n (cf. Eqs. (8) and (9)). One can then normalize these rates with those for RT. Note further that $\kappa_B/\kappa_S = 0.5835$ at all temperatures, so that one can combine these two into one effective rate $\kappa_{\text{eff}} = 1.5835 \kappa_S$. Thus, at room temperature, for an electron of 0.3 eV energy, combining stretching and bending, $-dE/dt = 8.71 \times 10^{11} \text{ eV s}^{-1}$. Figure 4 shows the variation of the rate of energy loss of a subvibrational electron with its energy during stage B at two temperatures respectively for excitation of the stretching and bending modes.

So far we have not considered the influence of molecular rotation to the degradation process which, in retrospect, turns out to be rather less important. This process, except for H_2 , is always mixed with elastic collision in all phases. Further, in the liquid, it is associated with various collective motions, such as hindered rotation, restricted translation and transverse acoustic modes [7]. The energy quantum is in the range of 10^{-2} – 10^{-3} eV [8]. Therefore, we have classified this in stage B in the appropriate far-IR spectral

Figure 5. Degradation times t_A (stage A) and t_B (stage B) as functions of T . Their sum is the thermalization time t_{th} .

region of $8\text{--}80\text{ cm}^{-1}$. Using Eq. (8) and experimental data for the absorption coefficient in this spectral region [7], we compute the cross-section for subvibrational electrons for this process as 0.396 Å^2 . The rate of cooling, by 'rotational' processes *only*, may now be computed as cross-section $\times$ energy quantum $\times$ scatterer density $\times$ average electron speed. We have used the rotational energy quantum of 10^{-3} eV , the full water molecule density and an average speed at 0.3 eV energy of a subvibrational electron. *Note that, for this process, the full molecular density must be used and not just the H-bond density as in the case of H-bond stretching and bending vibrations.* This, in the present case, gives a value

$$\text{Rotational cooling rate} = 0.0386 \times 10^{12} \text{ eV s}^{-1}, \quad (11)$$

which is generally small compared with that due to H-bond stretching and bending, evaluated at $0.871 \times 10^{12} \text{ eV s}^{-1}$ (vide supra). The total cooling rate during stage B is now computed as $0.9096 \times 10^{12} \text{ eV s}^{-1}$, which corresponds to a stage B time scale of $(0.5 - 0.0375)/0.9096 \times 10^{12} = 2.886 \times 10^{-13} \text{ s}$, taking the starting subvibrational energy of 0.5 eV and a room temperature kinetic energy of 0.0375 eV . Note that the rotational cooling rate in Eq. (11) remains constant at all temperatures, since the density effects in the rotational cross-section and energy loss rate cancel each other [cf. Eq. (8)].

Figure 5 shows the degradation time scales in stages A and B as functions of temperature. Their sum should be considered as the thermalization time. Note that both time scales increase slowly with temperature; however, t_B increases faster than t_A . Nevertheless, the thermalization time remains within the 10^{-13} s time scale up to $\sim 500\text{ K}$ and then increases by a factor ~ 2 around the critical temperature. The increases are due to the decrease of both the ordinary and H-bond density with temperature. The purpose of the present letter is to establish the nature of energy loss of subexcitation (stage A) and subvibrational (stage B) electrons in liquid water and thereby obtain the time scale of the two stages. Principal contributors for energy degradation are intramolecular vibrational excitation and dielectric interaction in stage A and H-bond vibrational excitations, stretching and bending, in stage B, combined with rotational excitation. In our earlier work with liquid *n*-hexane [3,4], the cross-sections of these low-energy interactions were adjusted to the free-ion yield at RT through the thermalization length and then the result was extended to higher temperatures. In the present work, for the first time, we have

derived the cross-sections directly from various experiments and then calculated the respective time scales.

In this letter we have not compared our results with experiments that have generated rather opposite temperature dependence of the spur size [23–26], which is intimately connected with thermalization length. This comparison will be attempted in a future publication [12]. Presently we note that, while some authors [23,26] have used different forms of density scaling resulting in an increase of thermalization length with T , others [24,25], using Monte Carlo simulation, argue for a decrease, attributable to excessive scattering of epithermal electrons, which is not easily understood. In any case, one would need elastic scattering cross-section to obtain a thermalization length from degradation time. Another important consideration is electron trapping, which, in the case of liquid hydrocarbons, is known to occur in the post-thermalization stage. Lukin [27] has pointed out the competition between geminate recombination and trapping for photo-generated electrons in water. This author has used very large elastic scattering cross-section by the trap due to resonance. We intend to address these problems in a later publication [12].

4. Conclusion

In this letter we have analyzed separately the contributions of intramolecular vibrational and dielectric interaction for energy loss of a subexcitation electron in liquid water, with energy below 5 eV , until the subvibrational level is reached. These rates are comparable at all temperatures, being $\sim 10^{13} \text{ eV s}^{-1}$, which is orders of magnitude smaller than that due to electronic excitation at higher energies. In the subvibrational regime, energy loss down to the thermal level is due to restricted 'rotation' and to H-bond vibrational excitation, whose contributions are not comparable except at the highest temperature. H-bond vibrational rate decreases with temperature and electron energy. H-bond bending contribution is not insignificant in this regime. Computed time scale in the subexcitation stage shows a small increase with temperature $\sim (0.83 - 1.50) \times 10^{-13} \text{ s}$. That due to 'restricted rotation' and H-bond vibrations, in the subvibrational stage, increases relatively rapidly with temperature, $\sim (2.89 - 13.23) \times 10^{-13} \text{ s}$, due to corresponding decrease of both H-bond and ordinary density.

Acknowledgments

This is document no. NDRL-5034 from the Notre Dame Radiation Laboratory which is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number: DE-FC02-04ER1553. Professor D. Swiatla-Wojcik of the Institute of Applied Radiation Chemistry, Łódź University of Technology, Poland is thanked for the data of the ordinary and H-bond density in water at room and higher temperatures.

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