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Cross sections, stopping powers, and energy loss rates for rotational and phonon excitation processes in liquid water by electron impact

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HIGHLIGHTS

- Cross sections in liquid water by electron impact of low energy were calculated.
- Rotational cross section in liquid phase are much less than those in gas phase.
- Energy loss rates depend significantly on the electron energy below 1 eV.

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ABSTRACT

We calculated cross sections, stopping powers, and energy loss rates for rotational and phonon-mode excitations caused by the impact of an electron in an energy region from 0.1 meV to 100 eV injected into liquid water. The spatial distribution of the decelerated electron depends on these cross sections. We performed calculations assuming an optical approximation with the dielectric functions that are experimentally reported in the literature. We observed that the cross sections lie below 1×10^{-16} cm^2 over the considered energy region. The values for rotational excitation processes in the liquid phase are less by three orders of magnitude than those in the gas phase because of the screening effect of neighboring water molecules on the interaction between the incident electron and water molecules. These results suggest that the cross sections in the liquid phase are significantly different from those in the gas phase. The values for phonon-mode excitations in the liquid phase are close to those reported for amorphous ice. Furthermore, we observed that the stopping power shows a maximum around 200 meV, and the energy loss rates, which are derived from the stopping power, depend significantly on the electron energy, particularly below 1 eV. The values obtained here will allow us to precisely estimate the decelerating process of an electron in liquid water to predict radiation effects such as chemical processes in water radiolysis or biomolecular damage induction strongly involved in low energy electron processes.

1. Introduction

The deceleration process of electrons ejected from water molecules in the liquid phase plays a significant role in the spatial distribution of those electrons, and thus determines subsequent chemical processes in water radiolysis or biomolecular damage induction in a living system exposed to ionizing radiation (Nikjoo et al., 1997; Tomita et al., 1997; Cobut et al., 1998; Yang et al., 2011). Electrons in water are gradually decelerated by imparting their energies to surrounding water molecules. The energy dispersal induces additional ionization as well as excitation of electrons, vibrational or phonon modes, and rotations through electron-molecular collisions. The deceleration process has thus far been studied using both theoretical and experimental approaches (Migus et al., 1987; Konovalov et al., 1988; Mozumder, 1988; Goulet and Jay-Gerin, 1988; Meesungnoen et al., 2002). Currently, programs for dynamical calculation of electrons in water have been developed to precisely calculate the spatial distribution of the electrons ejected by irradiation with various charged particles (Moribayashi, 2011; Kai et al., 2014). We have suggested that the spatial distribution of these electrons was significantly different from that of a subexcitation electron injected into water because of the effect of Coulomb fields of the parent cations (Kai et al., 2014). From that basis, we predicted that types of biomolecular damage

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could be modified via electron recapture by the cations. For the developed dynamical programs, cross sections of the gas phase were employed for calculations including the Coulomb interaction between all electrons and water cations, as well as electron-molecular collisions over hundreds of femtoseconds.

For the gas phase of water, a number of cross sections for many molecular processes have so far been reported by experimental and theoretical studies. Itikawa and Mason (2005) compiled a recommended set of cross sections in an energy region from 1 meV to 1 keV. For condensed phases, Michaud et al. (Michaud and Sanche, 1987a, 1987b; Michaud et al., 2003) experimentally reported cross sections of elastic and inelastic scattering for amorphous ice at 14 K in an energy region from 1 eV to 100 eV. The cross sections for rotational excitation were, however, not reported owing to experimental difficulties. On the other hand, dielectric function of liquid water was measured by inelastic x-ray scattering experiment above 7 eV (Hayashi et al., 2000). An optical approximation using dielectric functions derived from the theoretical and also experimental approaches has been generally employed to calculate the cross sections and stopping powers of electronic excitation and ionization processes in the liquid phase (Tomita et al., 1997; Ashley, 1982; Ashley, 1990; Nikjoo et al., 2006). Energy loss rates due to rotational, translational-phonon, and librational-phonon excitation in the liquid phase were also reported by a theoretical study in an energy region from 1 to 10 eV (Fröhlich and Platzman, 1953). Properties for phonon and vibration modes of liquid water were also measured by inelastic x-ray scattering experiments (Ruocco et al., 1996; Halcoussis et al., 2000). However, the dielectric functions or cross sections in those energy regions were not reported in their papers. To understand the electron deceleration process in liquid water, theoretical evaluations for the cross sections are indispensable. However, there still exists a considerable lack of cross section values for the liquid phase, particularly in the lower energy region below 1 eV, and, for this reason, a comprehensive analysis of electron thermalization has been difficult to perform.

To predict the chemical structure of biomolecular damage specific to the deceleration process of electrons in liquid water (Kai et al., 2014; Boudaïffa et al., 2000; Michael and O'Neill, 2000; Wang et al., 2009; Sanche, 2009; Oka et al., 2012), we establish values for the cross sections, stopping powers, and energy loss rates of electrons for liquid water assuming an optical approximation. The purpose of the present study is to calculate those quantities for electron impact in an energy region from 0.1 meV to 100 eV by considering the excitation processes of molecular rotation and phonon modes in the extremely low electron energy region with the aid of the dielectric functions recently obtained by Yada et al. (2008). We compare the absolute values and energy dependence of the obtained cross sections, stopping powers, and energy loss rates for liquid water with those for gas-phase water (Itikawa and Mason, 2005) and amorphous ice (Michaud et al., 2003) and discuss the differences between them.

2. Calculation method

The frequency of collision between an electron and a water molecule in a condensed phase is characterized by a dielectric function $\varepsilon(q,\omega)$, which is related to momentum transfer q and energy transfer ω of the electron (Lindhald, 1954). The energy absorption of liquid water and the screening effect (Michaud et al., 2003) of neighboring molecules on the interaction between the electron and water molecule are represented by $\mathrm{Im}(\varepsilon(q,\omega))$ and $|\varepsilon(q,\omega)|^2$, respectively, which are obtained from the dielectric function. The inverse mean free path $\lambda^{-1}(E)$, which determines the cross sections of electron-molecular collisions in a condensed phase in atomic units is given as follows (Lindhald, 1954):

$$\lambda^{-1}(E) = \int d\omega \tau(E, \omega), \tag{1}$$

where $\tau(E,\omega)$ is the differential inverse mean free path using the dielectric function. This function is derived as follows:

$$\tau(E, \omega) = \frac{1}{\pi E}\int_{q^-}^{q+} \frac{dq}{q}\mathrm{Im}\left(\frac{-1}{\varepsilon(q, \omega)}\right), \quad q^{\pm} = \sqrt{2}\left(\sqrt{E} \pm \sqrt{E-\omega}\right),$$

where E, q^+, and q^- are the incident electron energy, and maximum and minimum momentum transfers, respectively, and $\mathrm{Im}(-1/\varepsilon(q,\omega))$ is an energy loss function. The energy loss function $\mathrm{Im}(-1/\varepsilon(q,\omega))$ of the momentum transfer q has been given by an optical dielectric function $\varepsilon(0,\omega)$ at $q=0$ as follows (Ashley, 1990):

$$\mathrm{Im}\left(\frac{-1}{\varepsilon(q, \omega)}\right) = \int_0^{\infty} d\omega' \omega' \mathrm{Im}\left(\frac{-1}{\varepsilon(0, \omega')}\right)\frac{\delta\left(\omega - \left(\omega' + q^2/2\right)\right)}{\omega}. \tag{2}$$

Using Eqs. (1) and (2), and from considerations of electron exchange between an incident electron and a bound electron in a molecule, the inverse mean free path is finally expressed as follows (Ashley, 1990):

$$\lambda^{-1}(E) \approx \frac{1}{2\pi E}\int_0^{E/2} d\omega' \mathrm{Im}\left(\frac{-1}{\varepsilon(0, \omega')}\right) L\left(\frac{\omega'}{E}\right), \tag{3}$$

where

$$L(a) = (1-a)\ln\frac{4}{a} - \frac{7}{4}a + a^{3/2} - \frac{33}{32}a^2, \quad (a \ll 1).$$

In the same manner, the stopping power $S(E)$ of an electron in a condensed phase is given as follows (Ashley, 1990):

$$S(E) \approx \frac{1}{\pi E}\int_0^{E/2} d\omega' \omega' \mathrm{Im}\left(\frac{-1}{\varepsilon(0, \omega')}\right) G\left(\frac{\omega'}{E}\right), \tag{4}$$

where

$$G(a) = \ln\left(\sqrt{\frac{e}{8}}\frac{2}{a}\right) - \frac{3}{4}a - \frac{a}{4}\ln\frac{4}{a} + \frac{1}{2}a^{3/2} - \frac{a^2}{16}\ln\frac{4}{a} - \frac{31}{48}a^2,$$

for $e=2.71828$. The cross section $\sigma(E)$ and energy loss rate $R(E)$ are given by $\sigma(E)=\lambda^{-1}(E)N^{-1}$ and $R(E)=S(E)v$, respectively, where N is the number density, given as 3.0×10^{22} molecules/cm^3 of liquid water, and v is an amplitude of the velocity of an incident electron.

The optical dielectric function $\varepsilon(0,\omega)$ of liquid water derived from microwave and far-infrared spectroscopy measurements was reported by Yada et al. (2008), which was given in the following form:

$$\varepsilon(0, \omega) = \frac{\Delta\varepsilon_1}{1 + i\omega\tau_1} + \frac{\Delta\varepsilon_2}{1 + i\omega\tau_2} + \frac{A_T}{\omega_T^2 - \omega + i\omega\gamma_T} + \frac{A_L}{\omega_L^2 - \omega + i\omega\gamma_L} + \varepsilon_{\infty}, \tag{5}$$

where $\tau_1 = 1.08((T/228)-1)^{-1.73}$ ps, and the fitting parameters at a water temperature of $T=293$ K are $\Delta\varepsilon_1=74.9$, $\Delta\varepsilon_2=1.67$, $\tau_2=248$ fs, $A_T/(2\pi)^2=31.5$ THz^2, $\omega_T/2\pi=5.30$ THz, $\gamma_T/2\pi=5.35$ THz, $A_L/(2\pi)^2=108$ THz^2, $\omega_L/2\pi=14.7$ THz, and $\gamma_L/2\pi=8.08$ THz. The terms in Eq. (5) correspond to rotational modes (first and second terms), translational-phonon mode (third term), librational-phonon mode (fourth term), and dielectric constant in the high frequency limit $\varepsilon_{\infty}=2.0$ (fifth term).