Radiation Protection Dosimetry
Vol. 99, Nos 1–4, pp. 23–28 (2002)
Nuclear Technology Publishing

CROSS SECTION CALCULATIONS IN CONDENSED MEDIA: CHARGED PARTICLES IN LIQUID WATER

M. Dingfelder
Facultat de Física (ECM), Universitat de Barcelona
Av. Diagonal 647, E-08028 Barcelona, Spain

INVITED PAPER

Abstract — Ionisation cross sections for charged particles are deduced within the framework of the relativistic plane wave first Born approximation and the classical electromagnetic theory. The macroscopic dielectric response function is related to the atomic generalised oscillator strength. Interaction cross sections for proton impact on liquid water are presented and discussed. A semi-empirical model for the angular distribution of secondary electrons produced by proton impact on liquid water, which is based on the Bethe approach, is presented.

INTRODUCTION

Detailed Monte Carlo track structure simulation requires reliable cross sections for the interaction of radiation with atoms and molecules of the material under study. This kind of simulation uses the classical trajectory picture and follows the incident particle, as well as all produced secondary particles, from starting or ejection energies down to total stopping, by experiencing elastic and inelastic scattering events. Liquid water, which is the dominant component in the biological cell of soft tissue, is used as a model substance for organic matter.

The conventional theory used for describing excitation and ionisation of fast charged particles in matter is based on the plane wave (first) Born approximation (PWBA)[1,2]. This first order perturbation theory is expected to be valid only for sufficiently fast projectiles, with velocities much larger than the orbital velocities of the atomic electrons. The double differential cross section (DCS), differential in energy transfer E and 'recoil energy' Q, factorises in the PWBA in a purely kinematical factor and the generalised oscillator strength (GOS)[3]. The GOS completely characterises the response of the target atom or molecule in inelastic interactions within the PWBA and is independent of the projectile. In classical electrodynamics, the GOS is directly related to the dielectric response function (DF). Either the GOS is calculated from first principles for single atoms or molecules or the DF is modelled and fitted to experimental data for gases or dense media taking into account phase effects.

When a heavy charged particle (ion) slows down, electron capture and loss by the moving ion becomes increasingly important[4]. The projectile may change its charge state, excitation and ionisation probabilities may differ for the different charge states. The charge transfer process can produce residual target ions without ejecting secondary electrons, and secondary electrons can be ejected from the moving ion (or neutral atom) by the stripping process without ionising residual target atoms. All charge states as well as all charge changing processes contribute to the stopping cross section of a heavy charged particle. Cross sections are obtained from semi-empirical models usually based on experimental data.

This presentation focuses on proton impact on liquid water. A short summary on how total and differential cross sections for ionisations and excitations are calculated is given. Some comments on charge changing processes are made and their importance for slow heavy particle impact is stated. Emphasis is given to the angular distribution of the secondary electron emission spectrum, and a semi-empirical model based on the Bethe approximation is presented.

INTERACTION CROSS SECTIONS

Charged particles undergo different kinds of inelastic interactions with the matter. Detailed Monte Carlo track structure simulations[5,6] use the concept of the inverse mean free path (the macroscopic total cross section) to determine the kind and location of the next interaction. Information about the transfered and deposited energy in excitation or ionisation events is obtained from the corresponding DCSs.

Plane wave Born approximation

Excitation and ionisation cross sections are calculated within the framework of the relativistic first Born approximation. The effective Hamiltonian describes the interaction between the projectile (mass M, charge Z_0e, where e is the absolute value of the electron charge, kinetic incident energy τ) and the target (atomic number Z_1) as a first order perturbation. It is composed of a longitudinal part, which describes the instantaneous

Contact author E-mail: michael@ecm.ub.es

Coulomb interaction, and a transverse part, which accounts for the exchange of virtual photons. The projectile is represented as a Dirac plane wave, each atomic state of the target as a single Slater determinant constructed with orbitals that are solutions of the Dirac equation for a common central potential. Following the description of the PWBA given by Fano[2], the double DCS for inelastic collisions factorises in a purely kinematical factor and the GOS, df(Q,E)/dE, and reads

$$\frac{d^2\sigma^{(B)}}{dEdQ} = \frac{2\pi Z_0^2 e^4}{m_e v^2}\frac{1}{E}\left(\frac{1}{Q(1+Q/2m_ec^2)} + \frac{\beta_t^2}{(Q(1+Q/2m_ec^2)-E^2/2m_ec^2)^2}\right)\frac{df(Q,E)}{dE} \quad (1)$$

where $\mathbf{v}$ is the velocity of the projectile and β_t is the component of $\beta = \mathbf{v}/c$ perpendicular to $\mathbf{q}$,

$$\beta_t^2 = \beta^2 - \frac{E^2}{Q(Q+2m_ec^2)}\left(1+\frac{Q(Q+2m_ec^2)-E^2}{2E(\tau+Mc^2)}\right)^2 \quad (2)$$

The GOS fully characterises the target and is independent of the properties of the projectile. It only depends on the energy transfer E and the 'recoil energy' Q. Q is related to the momentum transfer $\mathbf{q}$ and is defined as $Q(Q+2m_ec^2)\equiv(cq)^2$. m_e is the electron rest mass. The GOS for the ionisation of atomic shells can be calculated from first principles. A more detailed description of the relativistic PWBA and the microscopic calculation of the GOS in the complete (Q,E) plane is given elsewhere[7]. In the non-relativistic limit ($c \rightarrow \infty$) the transverse part vanishes and Equation 1 reduces to the well known form, which is normally used in practical calculations.

Classical electrodynamics

An alternative starting point for the calculation of ionisation cross sections in a medium (atomic number Z_1, number of atoms per unit volume $\mathcal{N}$) is the classical electromagnetic theory. The target material is characterised by its dielectric response function (DF) $\epsilon(Q,E)$, depending only on energy transfer E and recoil energy Q. The DF is a complex valued function, its real ($\epsilon_1(Q,E)$) and imaginary ($\epsilon_2(Q,E)$) parts are related by Kramers–Kronig relations, which give rise to sum rules. $\epsilon(Q,E)$ can be modelled or directly obtained from experiment. The DCS again splits in a longitudinal and transverse part. The longitudinal DCS given by

$$\frac{d^2\sigma^{(L)}}{dEdQ} = \frac{2\pi Z_0^2 e^4}{m_e v^2}\frac{1+Q/m_ec^2}{Q(1+Q/2m_ec^2)}\frac{2Z_1}{\pi E_p^2}\,\mathrm{Im}\left(\frac{-1}{\epsilon(Q,E)}\right) \quad (3)$$

accounts for the interaction through the Coulomb field, screened by the polarisation of the medium, while the transverse part describes the part of the interaction associated to the vector potential. $E_p^2 = 4\pi\mathcal{N}Z_1\hbar^2e^2/m_e$ is the plasmon energy, and $\eta_2(Q,E) \equiv \mathrm{Im}(-1/\epsilon(Q,E))$ is the so-called energy loss function.

The longitudinal DCS, Equation 3, coincides with the longitudinal part (first term) of the microscopic PWBA DCS, Equation 1. The GOS, which is an atomic property, is related to the DF, which is a macroscopic property of the target material, in the following way:

$$\frac{df(Q,E)}{dE} \equiv E(1+Q/2m_ec^2)\frac{2Z_1}{\pi E_p^2}\mathrm{Im}\left(\frac{-1}{\epsilon(Q,E)}\right) \quad (4)$$

The transverse DCSs of both approaches only coincide in the low-density limit, $\mathcal{N} \rightarrow 0$, $\epsilon_1 \rightarrow 1$ and $\epsilon_2 \rightarrow 0$, i.e. for thin gases. In the non-relativistic limit ($c \rightarrow \infty$) the transverse parts vanish.

Total and energy transfer differential cross sections for proton impact on liquid water have been calculated recently[8] using the non-relativistic limit of Equation 3 and a modelled DF[9]. In that model, the imaginary part $\epsilon_2(E)$ of the DF is represented as a superposition of Drude-like functions in the optical limit ($Q = 0$) and fitted to optical reflectance measurements. The real part $\epsilon_1(E)$ is calculated from Kramers–Kronig relations. The momentum transfer dependence is added by an extension algorithm in the sense of an impulse approximation. The Bethe sum rule is fulfilled and the mean excitation value obtained from this model is 81.6 eV. A detailed description of the model as well as parameter sets can be found elsewhere[9]. Recently, new measurements of the energy loss function of liquid water using inelastic X ray scattering have become available[10]. Data for an energy transfer range from 0 to 100 eV at very low recoil energies (approximately 0) were presented. The new measurement looks promising to improve existing cross section data sets, and will possibly require refinements of the current models.

Slow particles

Inelastic processes like capture and loss of electrons become increasingly important when a heavy charged particle (ion) slows down, while the ionisation process dominates at higher energies. The charge state of the projectile remains unchanged in pure excitation or ionisation processes, but may change by picking up or losing its own electrons. Excitation or ionisation probabilities may differ for different charge states of a projectile. Cross sections σ_{ij} for changing from charge state i to charge state j used in Monte Carlo simulations are normally calculated using semi-empirical models which are usually based on experimental information and theoretical constraints, or represented by simple analytical functions, which reproduce the general trends of experimental data[8,11,12]. This includes also ionisation cross sections (σ_{ii} for the charge state i) for incident particle energies outside the validity of the PWBA. The PWBA is applicable for sufficient fast charged particles,

in particular, for electrons above approximately 500 eV and protons above 500 keV, respectively.

Semi-empirical cross sections for proton impact on liquid water have been derived recently. Two charge states of the projectile have been considered, the proton ($i = 1$) and the hydrogen atom ($i = 0$), while the third one, the negative hydrogen ion ($i = -1$) was neglected. Electron capture by the proton (σ_{10}) and electron loss of the hydrogen (σ_{01}) have been modelled by representing the cross sections by analytical functions orientating on experimental data of water vapour. These cross sections determine the probabilities Φ_i of finding the particle in charge state i. The probabilities Φ_0 and Φ_1 are displayed in Figure 1. As the electron capture cross section becomes dominant for particle energies below about 50 keV, the particle is dominantly found in the hydrogen atom state for low incident particle energies, while it remains in the proton state for high incident energies. Also displayed in Figure 1 are averaged probabilities Φ_0 and Φ_1 for the gas phase, derived from capture and loss cross sections for various molecular targets[4].

The probability Φ_1 is larger in the gas phase than in the liquid (condensed) phase, as already discussed[4]. Ionisation cross sections for both charge states have been derived from the semi-empirical Rudd model, excitation cross sections for protons from a Miller–Green model, while excitations by hydrogen atoms are neglected. Parameters for liquid water have been determined and adjusted by calculating stopping cross sections and comparing them with the ICRU recommendations for the different water phases and other experimental data. In the charge state approach, all inelastic processes of all charge states including the charge changing processes contribute to the stopping cross section. A detailed description of all semi-empirical models and parameters used for proton impact on liquid water is given in Reference 8.

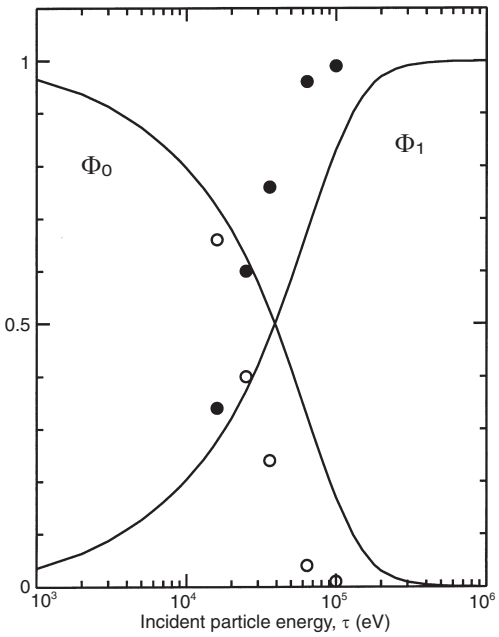

Figure 1. Probabilities Φ_1 and Φ_0 of finding an incident proton on liquid water either in the proton (1) or in the hydrogen atom (0) charge state versus the incident particle energy. Symbols represent averaged probabilities Φ_1 and Φ_0 for the gas phase[4].

ANGULAR DISTRIBUTION OF SECONDARY ELECTRONS

The angular distribution of electrons ejected with a given energy in inelastic collisions of heavy charged particles can be described as a superposition of contributions from 'soft' or glancing collisions (dipole interaction) and of contributions from 'hard' or binary collisions (binary encounter peak). The double DCS, differential in energy transfer E or secondary electron emission energy W and in the solid angle Ω, is given in the Bethe theory by

$$\frac{d^2\sigma}{dEd\Omega}(T,E) = \frac{16a_0^2 Ry Z_0^2 Z_1}{E_p^2}\frac{Ry}{T}\left[A(E,\theta)\ln\left(\frac{T}{Ry}\right) + B(E,\theta) + O\left(\frac{E}{T}\right)\right] \quad (5)$$

where T is the kinetic energy of an electron travelling with the same speed as the primary particle. In particular, the first term (including the $A(E,\theta)$ coefficient) represents the contribution from soft collisions, while the second ($B(E,\theta)$ coefficient) represents hard collisions. θ is the ejection angle of the secondary electron relative to the initial particle, the polar angle ϕ is distributed uniformly in the interval $(0, 2\pi)$. It is assumed that the angular distribution is normalised in order to reproduce the single differential cross sections determined earlier[9], when integrated over $d\Omega$.

Glancing term

Kim[13] pointed out a close relationship between the angular distributions of secondary electrons produced by photoionisation and by impact of fast charged particles. He showed that the dipole-interaction term (the glancing term) has essentially the same angular dependence as the photoelectrons ejected by unpolarised light, which is well known. Therefore, the angular dependence of the glancing term reads

$$A(E,\theta) = \frac{1}{4\pi}A(E)\left(1 + \frac{\beta_j}{2}P_2(\cos\theta)\right) \quad (6)$$

$A(E)$ is the usual Bethe coefficient, which is related to the dielectric response function in the optical limit[9], $P_2(x)$ the Legendre polynomial of the second order and β_j is the so-called asymmetry parameter. Theoretical

evaluation of β_j, however, depends on the model used to describe the target. Therefore, in the following, an empirical parameterisation for water vapour[14] is used, which reads

$$\beta_j = \begin{cases} 2 & \text{for s-like states} \\ \max(2(1 - \exp(0.168 - 0.024W)),0) & \text{else} \end{cases} \quad (7)$$

W here is the secondary electron energy in eV.

Hard collision term

In collisions of free charged particles the momentum transfer and the scattering angles are uniquely related by conservation of energy and momentum, and thus the angular distribution for a given momentum transfer is a δ function. For a bound electron, however, the residual ion absorbs parts of the momentum transfer and, therefore, the electron may be ejected in any direction. In 'hard' collisions the electron takes most of the transferred momentum and the angular distribution is sharply peaked in the direction of the momentum transfer. This is the so-called binary-encounter (BE) peak, which is, on a three dimensional plot, the Bethe ridge. The BE peak is fitted quite well by a Lorentzian in the cosine of the ejection angle. In the case of ion impact, electron transfer to the continuum has to be considered. These electrons are emitted in a forward direction with a secondary electron energy close to W = T. T is the energy for which the ejected electron has the same velocity as the primary ion. Therefore, the shape of the angular distribution is modified by an approximative factor, the so-called Salin factor F_S[15,16].

Finally, to sum up, the angular dependent hard collision term is given by

$$B(E,\theta) = N_\theta B(E) F_S(E,T,\theta) \left(1 + \left(\frac{\cos\theta - \cos\theta_{BE}}{\Delta\cos\theta_{BE}}\right)^2\right)^{-1} \quad (8)$$

B(E) is the usual Bethe coefficient, which is related to the dielectric response function in the optical limit[9] and N_θ is the normalising factor in respect to the solid angle $d\Omega$. The position of the BE peak, $\cos\theta_{BE}$ is determined by energy and momentum conservation and given by

$$\cos\theta_{BE} = \sqrt{\left(\frac{(\tau + Mc^2 + m_ec^2)^2}{(\tau + 2Mc^2)(E + 2m_ec^2)}\right)}\sqrt{\left(\frac{E}{\tau}\right)} \quad (9)$$

In the non-relativistic limit Equation 9 reduces to $\cos\theta_{BE,NR} = (M + m_e)/2M\ \sqrt{E/T}$. The width of the binary peak, $\Delta\cos\theta_{BE}$ is approximately given by[17]

$$\Delta\cos\theta_{BE} = \sin\theta_{BE}\Delta\theta_{BE} \approx \beta_{BE}\sqrt{(I/E)}\sqrt{(1 - \cos^2\theta_{BE})} \quad (10)$$

where I is the ionisation energy of the shell under consideration, and β_{BE} an empirical parameter ($\beta_{BE} \leq 1$), which accounts for the velocity distribution of the orbital electrons. In the following $\beta_{BE} = 0.8$ is chosen for liquid water. Finally, the Salin factor F_S[16] is given by

$$F_S(W,T,\theta) = \frac{2\pi\sqrt{I}\,[(T + W - 2\sqrt{(TW)}\cos\theta)^{-1/2} - T^{-1/2}]}{1 - \exp\{2\pi\sqrt{I}\,[(T + W - 2\sqrt{(TW)}\cos\theta)^{-1/2} - T^{-1/2}]\}} \quad (11)$$

Figure 2 shows model calculations of the secondary electron angular distributions for liquid water for different primary proton energies, obtained for various fixed secondary electron emission energies. In these calculations the BE peak position $\cos\theta_{BE}$ is multiplied by an additional empirical fine tuning factor δ_{BE}. This factor accounts for the momentum absorption by the target ions and is obtained from experimental data of water vapour[14]. It is parameterised as $\delta_{BE} = 1 + \exp(2.303a + b\ \log_{10}(\cos\theta_{BE,NR}))$ with $a = -2.50 + 2.270\ \exp(-1.066\ E_{ion})$ and $b = -1.25 + 0.635\ \exp(-1.375\ E_{ion})$. $E_{ion} = \tau$ is the incident particle energy in $MeV.u^{-1}$. With increasing emission energies W the BE peak develops clearly, the BE position coincides well with experimental data for water vapour[18]. In general, a fairly good agreement is found in the displayed energy range at small angles.

Stripping

Secondary electrons resulting from the stripping reaction of hydrogen atoms are emitted in a forward direction with a velocity similar to the velocity of the incoming particle. The angular distribution is modelled by a normalised Lorentzian $g_L(\theta)$ centered at $\cos\theta_{BE} = 1$ with a fixed width of $\Delta\cos\theta_{BE} \approx 0.1$.

ACKNOWLEDGEMENTS

M. D. thanks the European Community for the Marie-Curie Fellowship 'Low Energy Electrons in Microdosimetry and Health' under Contract No FIGD-CT-1999–50002. This work was partly supported by the European Community under Contract No FIGH-CT-1999–00005. The author wishes to express his appreciation to F. Salvat, J. M. Fernández-Varea, M. Inokuti and H. G. Paretzke for continuous discussions and much very valuable advice.

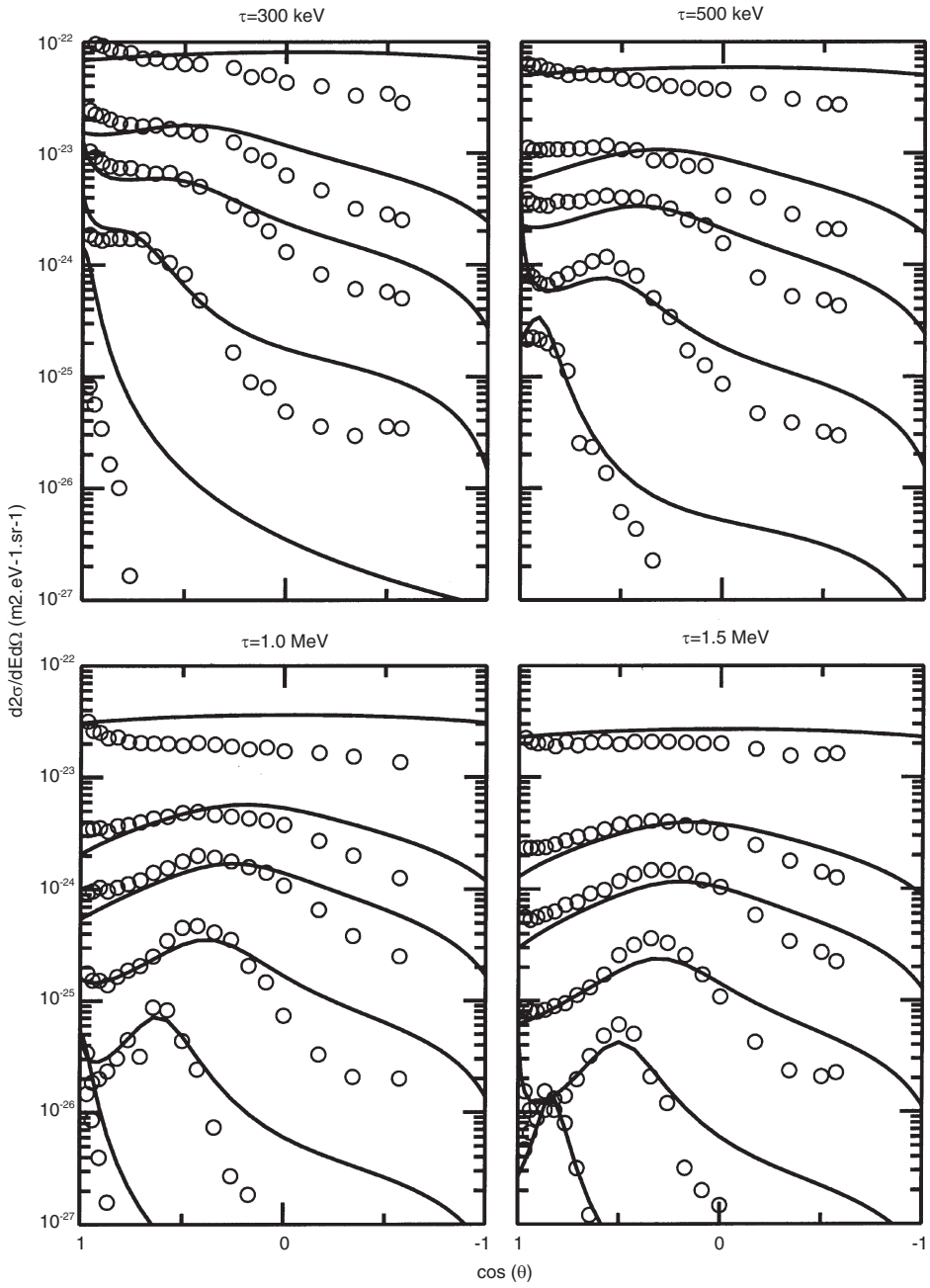

Figure 2. Double DCS for proton impact (with 300 keV, 500 keV, 1 MeV and 1.5 MeV kinetic energy, respectively) on water. Solid lines represent model calculations (this paper) for liquid water for fixed secondary electron emission energies (12 eV, 50 eV, 100 eV, 250 eV and 750 eV (additionally 2.2 keV for 1 Mev and 1.5 MeV proton impact only), from top to bottom, respectively); symbols represent experiments in water vapour[18] at the same secondary electron energies.

REFERENCES

1. Bethe, H. *Zur Theorie des Durchgangs schneller Korpuskularstrahlen durch Materie*. Ann. Physik (Leipzig) **5**, 325–400 (1930).
2. Fano, U. *Penetration of Protons, Alpha Particles and Mesons.* Ann. Rev. Nucl Sci. **13**, 1–66 (1963).
3. Inokuti, M. *Inelastic Collisions of Fast Charged Particles with Atoms and Molecules — The Bethe Theory Revisited*. Rev. Mod. Phys. **43**, 297–347 (1971).
4. Toburen, L. H. *Ionization and Charge-transfer: Basic Data for Track Structure Calculations*. Radiat. Environ. Biophys. **37**, 221–233 (1998).
5. Paretzke, H. G. *Radiation Track Structure Theory*. In: Freeman, G.R. (ed.) Kinetics of Nonhomogeneous Processes. (New York: John Wiley) pp. 89–170 (1987).
6. Ritchie, R. H., Hamm, R. N., Turner, J. E., Wright, H. A. and Bolch, W. E. *Radiation Interactions and Energy Transport in the Condensed Phase*. In: Glass, W. A. and Varma, M. N. (Eds.) Physical and Chemical Mechanisms in Molecular Radiation Biology. (New York: Plenum Press) pp. 99–135 (1991).
7. Segui, S., Dingfelder, M., Vernández-Varea, J. M. and Salvat, F. *The Structure of the Bethe Ridge. Relativistic Born and Impulse Approximations*. J. Phys. B: At. Mol. Opt. Phys. **35**, 33–53 (2002).
8. Dingfelder, M., Inokuti, M. and Paretzke, H. G. *Inelastic-collision Cross Sections of Liquid Water for Interactions of Energetic Protons*. Radiat. Phys. Chem. **59**, 255–275 (2000).
9. Dingfelder, M., Hantke, D., Inokuti, M. and Paretzke, H. G. *Electron Inelastic-scattering Cross Sections in Liquid Water*. Radiat. Phys. Chem. **53**, 1–18 (1998).
10. Hayashi, H., Watanabe, N., Udagawa, Y. and Kao, C.-C. *The Complete Optical Spectrum of Liquid Water Measured by Inelastic X-ray Scattering*. Proc. Natl Acad. Sci. **97**, 6264–6266 (2000).
11. Uehara, S., Toburen, L. H., Wilson, W. E., Goodhead, D. T. and Nikjoo, H. *Calculation of Electronic Stopping Cross Sections for Low-Energy Protons in Water*. Radiat. Phys. Chem. **59**, 1–11 (2000).
12. Uehara, S., Toburen, L. H. and Nikjoo, H. *Development of a Monte Carlo Track Structure Code for Low-energy Protons in Water*. Int. J. Radiat. Biol. **77**, 139–154 (2001).
13. Kim, Y.-K. *Angular Distributions of Secondary Electrons in the Dipole Approximation*. Phys. Rev. **6**, 666–670 (1972).
14. Wilson, W. E. and Nikjoo, H. *A Monte Carlo Code for Positive Ion Track Simulation*. Radiat. Environ. Biophys. **38**, 97–104 (1999).
15. Salin, A. *Ionization of Atomic Hydrogen by Proton Impact*. J. Phys. B **2**, 631–639 (1969).
16. Rudd, M. E. *Secondary Electrons from Charged Particle Collisions with Atoms and Molecules*. Nucl. Instrum. Methods B **56/57**, 162–165 (1991).
17. Rudd, M. E. *Differential and Total Cross Sections for Ionization of Helium and Hydrogen by Electrons*. Phys. Rev. A **44**, 1644–1652 (1991).
18. Toburen, L. H. and Wilson, W. E. *Energy and Angular Distributions of Electrons Ejected from Water Vapor by 0.3–1.5 MeV Protons*. J. Chem. Phys. **66**, 5202–5213 (1977).