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Ionization cross sections of water clusters as an alternative to liquid phase water : a Geant4-DNA simulation study

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ABSTRACT

Most of Monte Carlo Simulation (MCS) toolkits used to estimate the biological damage induced by radiations in cells consider these latter as composed of single water molecule. In this work, we used the Geant4-DNA MCS toolkit to evaluate the biological damage in cells modeled as clusters of water molecules instead of single water molecule. Increasing the number of molecules in water clusters enable to approximate liquid phase. Total cross sections for the ionization of small water clusters by electron impact are calculated. The first Born approximation is used to describe the collision dynamics where the incident and the scattered electrons are described by plane waves while the ejected electron is described by a Coulomb wave. Electrons belonging to the target molecule are described by a single-center molecular wave function. Using calculated cross sections, a scaling law and a universal curve are extracted to predict cross sections for the ionization of water clusters by single electron impact. These cross sections are implemented in Geant4-DNA to simulate the number of ionizations, mean-free path, range, stopping power, and the number of double and single strand breaks.

1. Introduction

Accurate determination of electron impact ionization cross section for molecular targets has gained large interest in the past years in various areas of physics and biology such as plasma physics, astrophysics, radiation physics and radiotherapy. These cross sections are also used in track structure codes such as Geant4 and its extension Geant4-DNA to simulate the process of electron impact ionization. Geant4-DNA can model the biological damage induced by ionizing radiation at the DNA scale, and accurate cross sections could significantly improve the accuracy of these simulations (1)(2)(3)(4)(5).

As biological medium (e.g. cells) are mainly composed of water (~ 70%), water molecule cross sections are considered as a good approximation for the modeling of particles' interactions within. The ionization cross sections for liquid water used in Geant4-DNA are calculated using DNA are based on the plane wave Born approximation (6), or obtained from the CPA100 Monte Carlo track structure code where the Binary Encounter Bethe (BEB) has been used for the ionization by electron impact (7)(8). Calculated values are then compared to measurements so the accuracy of theoretical model can be evaluated. Unfortunately, ionization cross sections by electron impact can not be measured in neither liquid nor solid phase of water and have been obtained for vapor phase only (9)(10)(11)(12)(13)(14)(15).

In most theoretical and experimental data, liquid water is represented as a single molecule (H₂O). In order to be realistic, liquid water should be considered as a group of water molecules (i.e. clusters) held together by hydrogen bonds

(16)(17). In addition, as it is shown in (18) (19) (20) (21), water clusters constitute an excellent intermediate between the diluted phase and the condensed phase. Therefore, their cross sections must be calculated in order to mimic particles' interactions in the environment of a condensed phase water molecule.

In this work, total cross sections for the ionization of water (H₂O) and small water clusters (H₂O)_n with n=2-4 by single electron impact are calculated with the BEB model (22)(23) and the first Born approximation using a Coulomb Wave (FBA-1CW) to describe the ejected electron and a plane wave for the incident and scattered electrons. A single-center molecular wave function was used to describe the electron of the target molecule(24)(25). Moreover, we propose to calculate the cross sections of clusters of n molecules by scaling the values obtained for one molecule with the mean cluster radius obtained via the *Gaussian* software. These cross sections are then implemented in Geant4-DNA and the number of ionizations, mean-free path, range, stopping power, single strand breaks (SSB), and double strand breaks (DSB) are calculated for each water cluster to show that the biological effects induced by the ionizing radiation could change as a function of the water cluster size. Geant4 version 11.0.1 is used in this work.

To our knowledge, this study is the first of its kind in the field. The structure and stability of water clusters has been investigated in (16) and their geometry is provided from the Cambridge Cluster Database (17). Calculations for condensed water medium may also be performed by ab initio calculations (26). The molecular orbitals for the FBA-1CW Model are generated using the Gaussian 09 program (27) with the 6-31G basis set at the Restricted Hartree-Fock (RHF) level of theory. The calculation is done on the High

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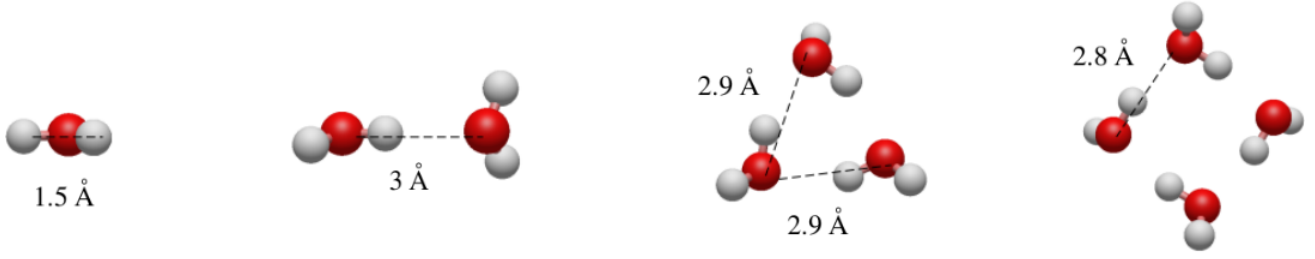


Figure 1: Geometry of 1, 2, 3 and 4 water molecules respectively provided from the Cambridge Cluster Database (17) and Avogadro software.

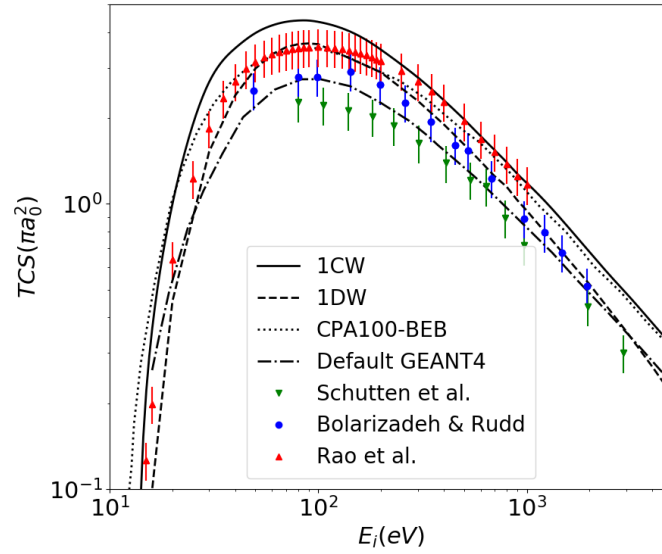


Figure 2: Total ionization cross sections of H_2O calculated with the 1CW model (solid line) and the 1DW model (dashed line) as a function of the incident electron energy. The experimental ionization cross sections presented are those of Schutten et al (1966) (9) (solid down triangles), Bolarizadeh and Rudd (1985) (11) (solid circles), and Rao et al (1995) (14) (solid up triangles). The Geant4-DNA cross sections presented here are calculated using Bethe's theory (dotted line) or obtained from the CPA100 Monte Carlo track structure code (7)(8) (dash-dotted line).

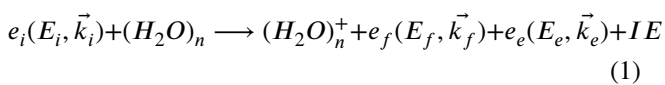
Performance Computing Center of the University of Strasbourg using the Message Passing Interface (MPI) technique to reduce the computing time.

2. Method

Total Ionisation Cross sections are calculated using the FBA-1CW and the Binary-Encounter-Bethe models. The two models are briefly described below. For further details, one could refer to (22), (23), (24) and (25), .

2.1. FBA-1CW Model

The ionization by single electron impact of water clusters $(H_2O)_n$, where n is the number of water molecules, can be represented by:



where E_i, E_f, E_e and $\vec{k}_i, \vec{k}_f, \vec{k}_e$ represent respectively the energies and momenta of the incident, scattered (final state of the primary electron) and ejected electrons and IE is the ionization energy of the orbital from which the electron is ejected.

The probability of this interaction can be determined over the range of ejected electron angles by calculating the triple differential cross section (TDCS). In the FBA and for a particular orientation of the molecule defined by Euler angles α, β, γ , the TDCS for the ionization by single electron impact is given by:

$$\sigma^{(3)}(\alpha, \beta, \gamma) = \frac{2}{(2\pi)^5} \frac{k_f k_e}{k_i} |\langle \Psi_f | V | \Psi_i \rangle|^2 \quad (2)$$

where Ψ_i is the initial state and Ψ_f is the final state. V is a purely Coulomb interaction potential between the projectile and the target. It can be written as a sum of two terms; $V_{e_i, k}$

and V_{e_i, e_j} , which represent the interaction of the incident electron e_i with respectively the k^{th} nucleus of the target and the j^{th} bound molecular electron.

$$V = V_{e_i, k} + V_{e_i, e_j} = \sum_{k=1}^{N_{atoms}} \frac{Z_k Z_{e_i}}{|\vec{R} - \vec{R}_k|} + \sum_{j=1}^{N_{electrons}} \frac{Z_{e_j} Z_{e_i}}{|\vec{R} - \vec{r}_j|} \quad (3)$$

where \vec{R} , \vec{R}_k , and \vec{r}_j are the position vectors of respectively the heaviest nucleus with respect to the incident electron, the k^{th} nucleus with respect to the heaviest nucleus, and the j^{th} bound electron with respect to the heaviest nucleus.

In the plane-wave Born approximation the initial and final states are written as $\Psi_i = \varphi_i \times \phi_i$ and $\Psi_f = \varphi_f \times \mathcal{F}_{\vec{k}_e}^{(-)}$ where the incoming φ_i and scattered electrons φ_f are both described by plane waves. The ejected electron wave function $\mathcal{F}_{\vec{k}_e}^{(-)}$ is described by either a Coulomb wave in the 1CW model or by a distorted wave in the 1DW model.

The molecular wave functions ϕ_i are generated using Gaussian09 (27) with the 6-31G basis set at the RHF level of theory. Gaussian09 is a software package used for quantum chemistry calculations. It's designed to perform a variety of computational tasks related to the electronic structure of molecules. In our work, the Gaussian 09 quantum chemistry software enables us to generate molecular wave functions for any molecule directly from the output file it provides. To simplify the study of multi-center molecules we perform a single-center partial wave expansion of the molecular wave function. A detailed description of the single-center spherical Gaussian functions was given in (24) (28) and this methodology was used in many studies (29; 30; 31; 32; 33; 34; 35; 36).

Based on the development above, the TDCS (averaged over all molecular orientations) of the i^{th} molecular orbital finally becomes:

$$\sigma^{(3),i} = \frac{k_f}{k_e k_i} \frac{64}{k^4} \sum_{\lambda, m_\lambda} \sum_{\mu} \frac{1}{\hat{\lambda}} |S_{\lambda, m_\lambda, \mu}^i|^2 \quad (4)$$

with

$$S_{\lambda, m_\lambda, \mu}^i = \sum_{l_e, m_e} \sum_l (-1)^\mu i^{l-l_e} e^{i\delta_{l_e}} Y_{l_e, m_e}(\hat{k}_e) Y_{l, \mu-m_e}(\hat{k}) A_{l_e, m_e, l}^{\lambda, \mu} \times R_{l_e, l, \lambda, m_\lambda}^i \quad (5)$$

$$A_{l_e, m_e, l}^{\lambda, \mu} = (\hat{l}_e \hat{\lambda})^{\frac{1}{2}} \begin{pmatrix} l_e & l & \lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_e & l & \lambda \\ -m_e & m_e - \mu & \mu \end{pmatrix} \quad (6)$$

and

$$R_{l_e, l, \lambda, m_\lambda}^i = \int_0^\infty r^2 \tilde{R}_{\lambda, m_\lambda}^i(r) \frac{F_{l_e}(k_e r)}{r} (j_l(kr) - \delta_{l0}) dr, \quad (7)$$

where $\hat{\lambda} = 2\lambda + 1$, $\vec{k} = \vec{k}_i - \vec{k}_f$ is the momentum transfer, and $\tilde{R}_{\lambda, m_\lambda}^i$ is the radial part of the (λ, m_λ) component of the partial wave expansion of the molecular orbital i .

The double differential cross section (DDCS) can be calculated from the TDCS by integrating it over the solid angle of the ejected electron:

$$\sigma^{(2),i}(\Omega_f, E_e) = \int \sigma^{(3),i}(\Omega_f, \Omega_e, E_e) d\Omega_e = \left(\frac{d^2\sigma}{d\Omega_f dE_e} \right)^i \quad (8)$$

Hence, the analytical form of the DDCS is:

$$\sigma^{(2),i}(\Omega_f, E_e) = 2 \times \frac{8}{\pi} \frac{k_f k_e}{k_i} \frac{1}{q^4} \sum_{\lambda, m_\lambda} \sum_{l_e, l} \hat{l} \hat{l} \begin{pmatrix} \lambda & l_e & l \\ 0 & 0 & 0 \end{pmatrix}^2 \times [R_{l_e, l, \lambda, m_\lambda}^i]^2 \quad (9)$$

Integrating the DDCS numerically over the scattered electron solid angle yields the simple differential cross section (SDCS):

$$\sigma^{(1),i}(E_e) = \int \sigma^{(2),i}(\Omega_f, E_e) d\Omega_f = \left(\frac{d\sigma}{dE_e} \right)^i \quad (10)$$

Finally, the total cross section (TCS) for each orbital can also be determined by numerically integrating the SDCS over the ejected electron energy:

$$\sigma^i = \int_0^{E_i - I E} \left(\frac{d\sigma}{dE_e} \right)^i dE_e \quad (11)$$

The total cross section σ for the molecule is the sum of the cross sections σ^i over all occupied orbitals.

2.2. Binary-Encounter-Bethe (BEB)

The BEB model for calculating electron-impact ionization cross sections was developed by Kim and Rudd in 1994 (22)(23). The BEB model provides a simple and easy-to-use formula for the ionization cross section. Only the binding energies B and kinetic energies U of the orbitals of the target are required. The BEB cross section for ionization of orbitals at an incident electron energy T is given by:

$$\sigma_{BEB}^i = \frac{S}{t + u + 1} \left[\frac{\ln t}{2} \left(1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} - \frac{\ln t}{t + 1} \right], \quad (12)$$

where $t = T/B$, $u = U/B$ are normalized incident and kinetic energies, $S = 4\pi a_0^2 N R^2 / B^2$, $a_0 = 0.53\text{\AA}$, $R = 13.61 \text{ eV}$, N : the number of electrons in an atomic or molecular orbital.

2.3. Scaling law for clusters with n molecules

The calculations of cross sections is complex and time consuming especially for large molecules. To overcome the heaviness of calculations, we proposed a scaling law that enables the cross sections' calculations of a n water molecules cluster from a single water molecule without actually doing the detailed calculations. The scaling factor is the mean square radius $\langle R^2 \rangle$ representing the spatial expansion

of the water cluster as given by the Gaussian toolkit. A universal curve with the equation below (related to the Lotz formula (37)) can be used to simplify the calculation.

$$y(x) = A \times \frac{\ln\left(\frac{x}{B}\right)}{x + C} \quad (13)$$

where x is the variable and A , B and C are fitting parameters.

2.4. Implementation in Geant4-DNA

Same steps as in the ICSD (Ionization Cluster Size Distribution) example of Geant4-DNA were followed to use the cross sections of water clusters. In this example, new DNA-like material's cross-sections are used to calculate the number of ionisations per event in a small cylinder mimicking a micro volume of chromatin. The PhysicsList in the ICSD example shows how to use the new classes, such as G4VDNAModel and G4DNAModelInterface, that allow Geant4-DNA to model electron track in materials other than liquid water (38). The new cross sections were implemented in Geant4-DNA with a new model class inherited from the G4VDNAModel class to simulate the ionization by electron impact of the new materials. Water clusters were defined as new materials in the DetectorConstruction class with a density equal to $1g/cm^3$, their elements (Hydrogen "H" and Oxygen "O") are added using the AddElement(element, numberOfAtoms) function. Their cross sections are implemented in tables in Geant4-DNA. These cross sections are read in the PhysicsList class using the new physics model class inherited from the G4VDNAModel class. The AddCrossSectionData(materialName, particleName, fileCS, fileDiffCS, scaleFactor) function is used to add the cross sections of these new materials. The cross sections of water clusters are passed to this function through the fileCS (Total Cross section) and the fileDiffCS (Differential Cross Sections) parameters. This function is defined in the G4VDNAModel class and called in the physics model class. In the physics model class, there are also functions to read the cross section tables, use interpolation methods and give the cross section for a given energy and orbital, and sample the secondary electrons, etc. The new physics list is used in ICSD, spower, range, and Clustering (39) examples of Geant4-DNA to study the number of ionization, stopping power, range, SSB and DSB as a function of the cluster size.

3. Results

3.1. Cross Sections

Total cross sections of one water molecule are first calculated with the 1CW and 1DW models and compared to experimental and Geant4-DNA cross sections. The results are shown in Figure 2. Cross sections are calculated in πa_0^2 unit where a_0 is the Bohr radius equal to 5.3×10^{-11} m.

The 1DW model is extremely time consuming due to the high number of partial waves required. Therefore, the cross sections presented below are calculated using only the 1CW model.

The cross sections of 1, 2, 3 and 4 water molecules calculated with the 1CW and BEB models are shown in Figure 3 and Figure 4 respectively.

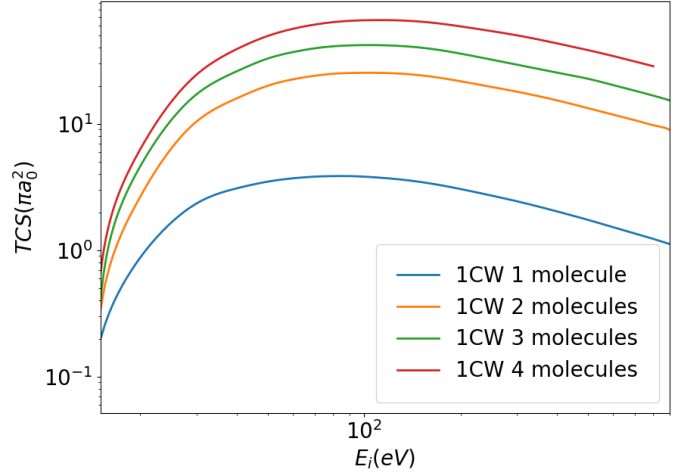


Figure 3: Total cross sections (in πa_0^2) of water clusters calculated with 1CW model as a function of the incident electron energy.

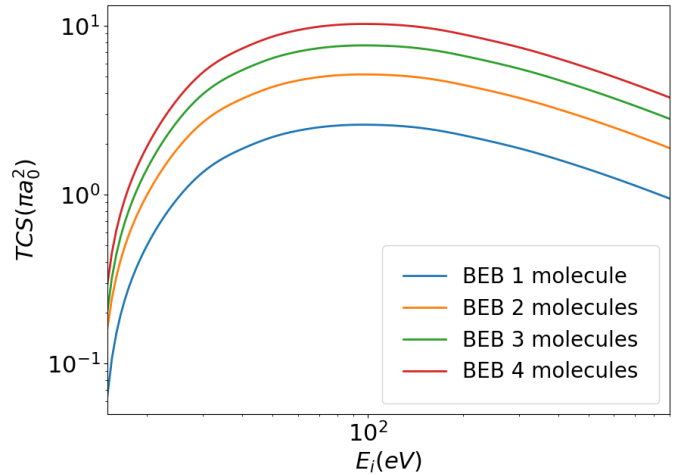


Figure 4: Total cross sections (in πa_0^2) of water clusters calculated with BEB model as a function of the incident electron energy.

Figure 5 represents the variation of the SDCS calculated using 1CW model at different incident energies as a function of the electron ejected energy.

3.2. Scaling Law and universal curve

Figure 7 represents the universal curve compared to the TCS of water clusters for $n = 2, 3$ and 4 molecules divided by the scaling factor $\langle R^2 \rangle$. The variation of the scaling factor $\langle R^2 \rangle$ (in atomic unit) with respect to the number of water molecules is shown in Figure 6. From equation 13 and Figure 6, the total cross section can be expressed as follows:

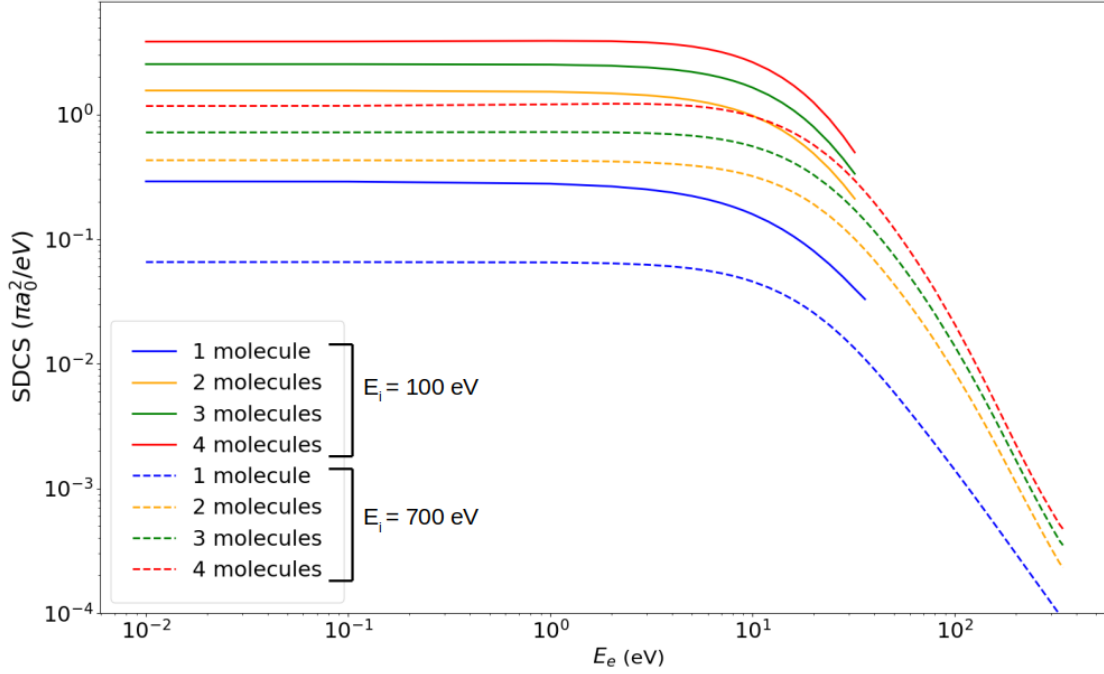


Figure 5: Single Differential Cross Sections of water clusters, for $E_i = 100$ and 700 eV, as a function of the ejected electron energy.

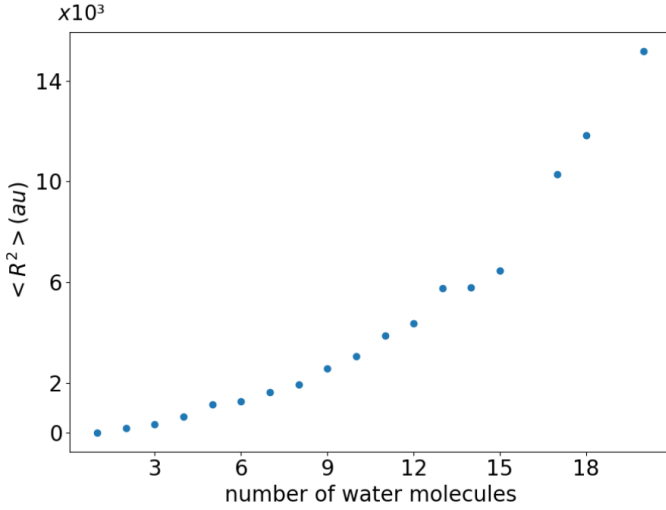


Figure 6: $\langle R^2 \rangle$ in atomic unit (au) as a function of the number of molecules within the cluster.

$$\sigma = A \times \langle R^2 \rangle \times \frac{\ln\left(\frac{E_i}{B}\right)}{E_i + C} \quad (14)$$

with $A=11.68$, $B=16.54$ and $C=88.85$;
 σ is the total cross section in unit of πa_0^2 ;
 E_i is the energy of the incident electron in eV.

This scaling law can also be applied for SDCS data (Figure 8).

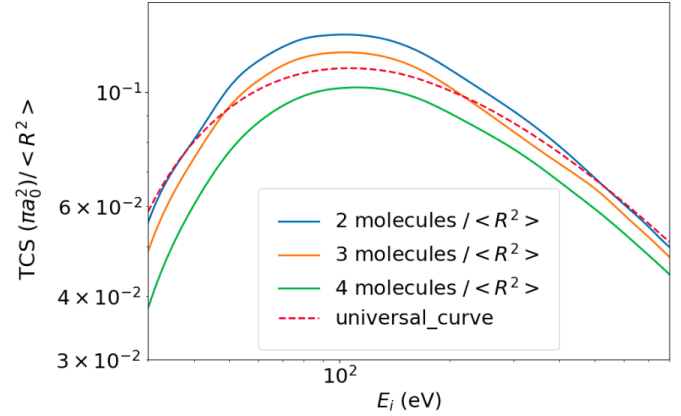


Figure 7: The universal curve (dashed line, formula 14 divided by $\langle R^2 \rangle$) for the ionization cross sections of water clusters compared to the curves of cross sections divided by $\langle R^2 \rangle$.

3.3. Simulations with Geant4-DNA

Finally, to study the impact of the use of water clusters cross sections on the simulation of biological damage, our 1CW cross sections are implemented in Geant4-DNA as classes of Geant4-DNA physics models inherited from the G4VDNAModel class for electron impact ionization process.

Cross sections obtained from our model are used to study the variation of mean-free path "mfp", stopping power, range, number of ionization, double and single strand breaks as a function of the cluster size. The mfp, stopping power, and range presented in Figure 9, 10 and 11 respectively are

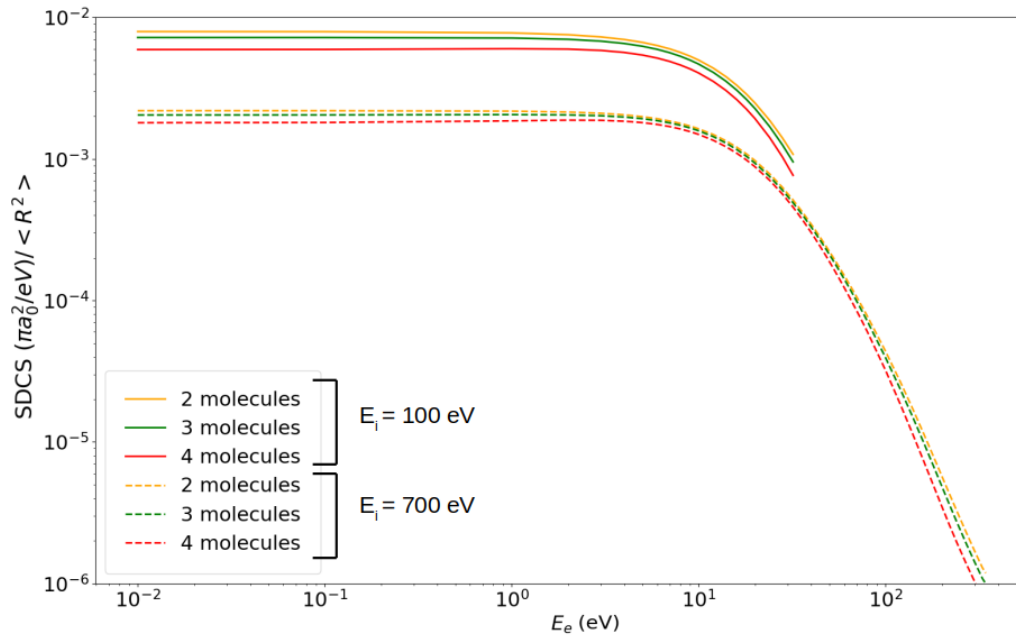


Figure 8: SDCS of water clusters divided by $\langle R^2 \rangle$.

calculated in a 1 m radius sphere.

The mean number of ionizations per event (Figure 12), induced by 1000 events of electrons with an energy of 500 eV, is calculated in a small cylinder of 2.3 nm diameter and 3.4 nm height that is centered in a cubic world of 10 nm side length filled with liquid water (same geometry as in the ICSD example of Geant4-DNA). The cylinder is filled with water cluster material. The mean number of ionizations is also calculated for a larger volume geometry that is ten times larger than the original geometry, and presented in Figure 13. On the other hand, the mean number of strand breaks 14 are calculated in a target box of $1\mu\text{m} \times 1\mu\text{m} \times 0.5\mu\text{m}$ as in clustering example of Geant4-DNA. The Target box is made of water clusters materials. The density used is the density of liquid water equal to 1 g/cm^3 .

These examples are modified to simulate electron tracks in water clusters using our new model for the ionization process and Geant4-DNA models for the rest of processes. The error bars in these figures correspond to the statistical variations between simulations outputs performed using different random seeds.

4. Discussion

The cross sections presented in the previous section show a strong molecular size dependence. Obviously larger molecules induce higher interaction probability and consequently higher total and differential cross sections (Figure 3, 4 and 5). These results emphasize the importance of using accurate cross sections of bio-molecules in the simulation of biological damage.

There are no studies that calculated cross sections for ionisation of water clusters by electron impact. Therefore,

the 1CW and 1DW cross sections of single water molecule were calculated and compared to experimental and Geant4-DNA cross sections (Figure 2). The 1CW model shows a good agreement with Rao et al and CPA100 data at incident energies higher than 250 eV. On the other hand, the 1DW shows better agreement with Rao et al and CPA100 data over the whole energy range, and also with Bolarizadeh and Rudd data at high incident energies. In the 1DW model, the short-range interaction between the ejected electron and the ionized target is explicitly taken into account. Furthermore, the use of distorted waves for the incident electron is expected to improve the agreement with experimental data especially for low incident energies.

The 1DW model takes more computation time and resources than the 1CW model. Therefore, the 1CW model is used in this work to calculate the water clusters cross sections. This model was able to give cross sections relatively in good agreement with the experimental cross sections of single water molecule and allows to obtain logical trends in terms of the number of molecules.

The water clusters cross sections calculated with the 1CW and BEB models in Figure 3 and Figure 4 shows that the cross sections increase with the increase in the number of molecules while maintaining the same shape with respect to the energy of the incident electron. Figure 4 shows that the BEB cross sections of a water cluster can be calculated by simply multiplying the cross sections of one water molecule by the number of molecules in this cluster. The 1CW cross sections are higher than those of BEB. The observed discrepancies can be attributed to the difference between these models.

As previously mentioned, the calculation of cross sections is heavily time and resource consuming. For a cluster

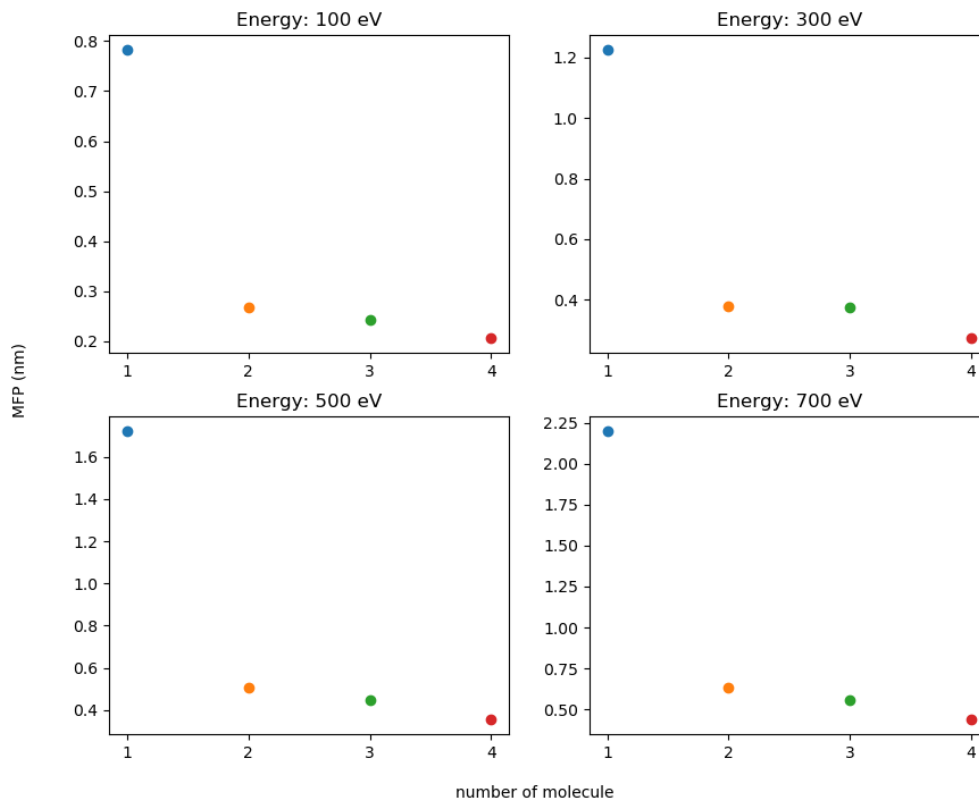


Figure 9: The mean-free path (in nm) as a function of the number of molecules in the the cluster plotted for electron energies of 100, 300, 500, and 700 eV.

of 4 water molecules for example, it takes about 12500 cpu hours for each incident energy, i.e. 25 hours with 500 processors. Cross sections calculation for a water cluster with a higher number of molecules is more computationally expensive. Due to limited resources, we could not repeat these calculations for a larger cluster. The search for a universal curve and a scaling law was extremely useful for this case. The mean square radius $\langle R^2 \rangle$ of the water clusters was the most logical quantity to use as a scaling law for the water clusters cross sections calculated with the 1CW model since there is a direct molecular size dependence of the calculated cross sections and the $\langle R^2 \rangle$ describes the electronic spatial extent of the molecules. The universal curve found and presented in Figure 7 allows to estimate the 1CW total cross sections of a water cluster by multiplying it by $\langle R^2 \rangle$.

The aim of this work was to study the effect of using water clusters cross sections, calculated in the same framework with the same model and the same parameters, on the simulation of biological damage. Therefore, the 1CW cross sections of water clusters are implemented in Geant4-DNA. The equation extracted from the universal curve (equation 14) can simplify the implementation. Using this equation with the TCS table of single water molecule in Geant4-DNA,

we can simulate the ionization of a n water molecules cluster by simply changing $\langle R^2 \rangle$ according to the number of molecules within the cluster.

Stopping power and range calculations for single water molecule material show a good agreement with the "option6" physics models of Geant4-DNA. These quantities change as a function of the number of molecule in the cluster. The mfp presented in Figure 9 decreases as a function of the number of molecule in the cluster. The reduction in the mfp, which is the average distance a particle can travel before experiencing an interaction, leads to a higher probability of interaction. The change in the number of ionizations as a function of the number of molecules was expected (Figure 12). As the cross sections increase with increasing number of molecules, the mfp decreases, the probability of ionization increases and therefore the number of ionizations increases. To ensure that the observed increase is not due to changes in the geometry of the system, we repeated the simulations using a larger volume. The Figure13 shows that the ionization number also increases as the number of molecules increases in the larger volume. However, the difference in the ionization number between each cluster in the larger volume is smaller than that observed in smaller volumes, and these values become increasingly similar to

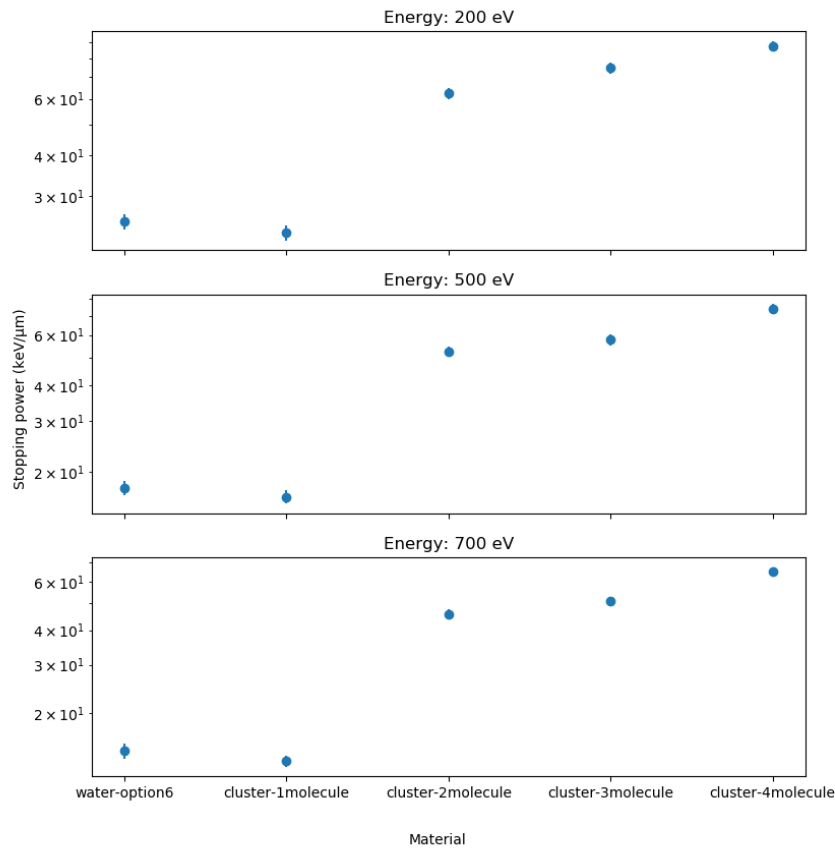


Figure 10: The stopping power as a function of the number of molecules in the cluster plotted for electron energies of 200, 500, and 700 eV.

each other. Anticipated changes in the simulation are likely to impact the chemical processes involved. An increase in the probability of ionization is expected to result in a higher number of electrons being ionized in the medium, which will boost the chemical reactions. Therefore, this work should be coupled with a chemical study to evaluate the effect of the use of water clusters materials on the chemical step of the simulation. The simulation of biological damage using these new cross sections shows that changing the cross sections will induce changes in the simulation results. Using more condensed material, in the same target volume with the same kinematic parameters, leads to an increase in the DSB and a decrease in the SSB (Figure 14).

5. Conclusion

In this paper we present the cross sections of water clusters calculated with the ICW and BEB models. It has been demonstrated that there exists a scaling law and a universal curve that facilitate the calculation. The cross sections were implemented in the Geant4-DNA simulation toolkit and the strand breaks are simulated. The results show that the obvious differences of ionization cross sections

between water clusters and single water molecule affect the radiation damage estimation and, therefore, the importance of accurate simulation of these data. This work could be coupled with a chemical study to evaluate the effect of the use of water clusters on the chemical step of the simulation. The use of these cross sections in the treatment planning systems (TPS) can improve simulations of biological damage induced by ionizing radiation and subsequently establish more effective treatment plans. In this study, our primary focus was on investigating water clusters as an initial step in modeling liquid water. For future work, to understand the behavior of a single water molecule in the liquid phase, we have to extract the cross sections of the five orbitals specific to the water molecule and the remaining orbitals will be considered as representative of the surrounding environment. This approach enables us to derive the cross sections of a water molecule in the liquid phase, taking into account its interaction with neighboring water molecules.

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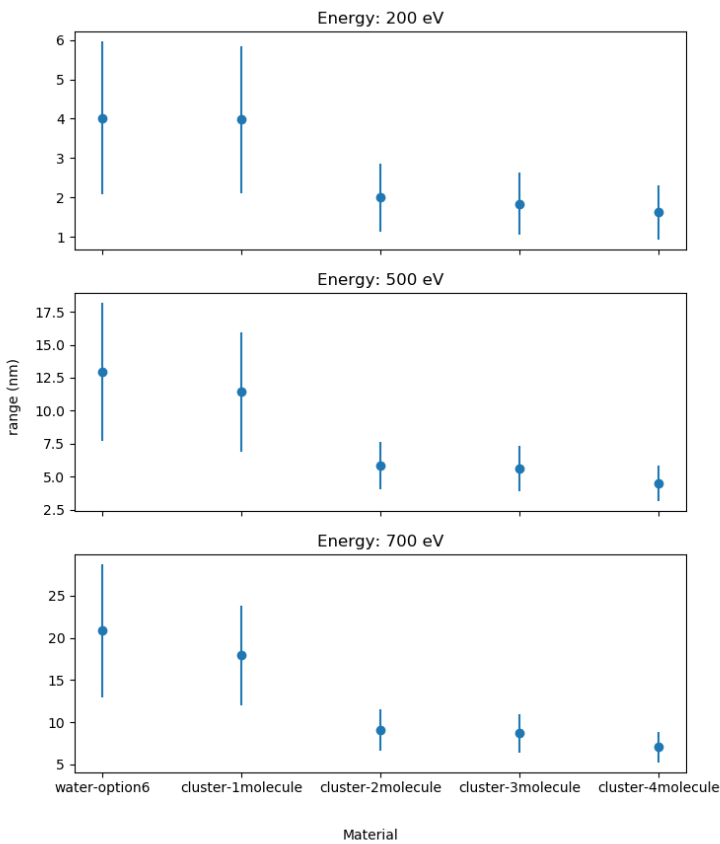


Figure 11: The penetration range as a function of the number of molecules in the cluster plotted for electron energies of 200, 500, and 700 eV.

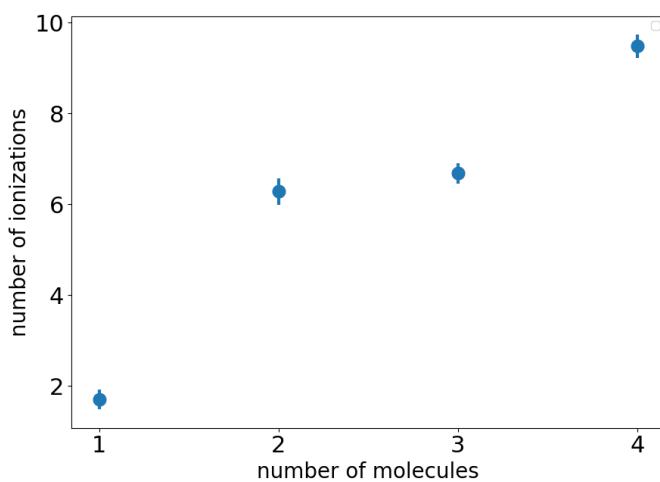


Figure 12: The mean number of ionizations per event as a function of the number of molecules within the cluster.

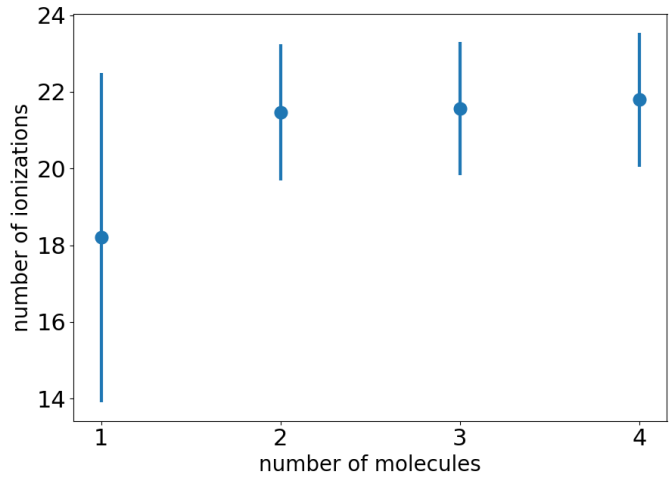


Figure 13: The mean number of ionizations per event as a function of the number of molecules within the cluster for larger volume.

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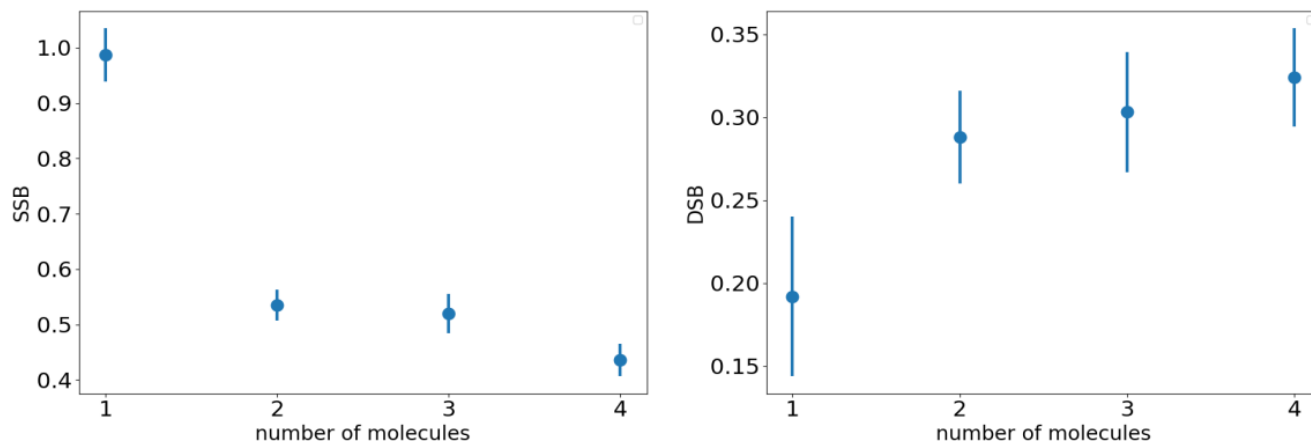


Figure 14: Electron induced SSB (left) and DSB(right) obtained as a function of the number of molecules within the cluster.

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