

Article

Liquid Water Ionization by Energetic Electron Impact

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Abstract

We theoretically study the single ionization of liquid water by impact of fast electrons. A realistic description of the wavefunction for an isolated water molecule in the liquid phase is obtained by means of a Wannier orbital formalism. In this way, we consider ionization from the most external orbitals $1B_1$, $2A_1$, $1B_2$ and $1A_1$ of a single liquid water molecule. Triple, double, single differential and total cross sections are computed through a first order model with proper Coulomb conditions for the ionized electron. We compare our calculations with measurements and other theoretical results for liquid and gaseous phases. An analysis of the main features of the cross sections is performed. Previous theoretical works found almost no discrepancies between these observables in spite of the physical dissimilarities of both phases. In this work, we compare our results with other theories and with the available experiments for vapor. We report interesting differences between the differential and total cross sections of the mentioned phases.

Keywords: liquid; water; ionization

1. Introduction

The ionization of water is a fundamental reaction in various fields, including plasma physics, cooling systems in fusion research, and astrophysics. As liquid water is the primary component of living matter, the ionization of water molecules in the liquid phase is of significant interest in radiobiology and medical physics. In passing through biological tissue, ionizing radiations trigger reactions involving water molecules that produce ejected (or secondary) electrons, protons, hydroxyl radicals, etc. Among them, secondary electrons produced during the impact of fast electrons are of utmost importance in biological radiation applications, because they play a crucial role in the mechanisms that lead to cell mutation and death [1]. The lethality of the radiation is closely related to the angular and energy distributions of these secondary electrons, determining the energy dose deposited in the biological medium. Therefore, many track structure studies based on computer simulations require the cross sections for ionization of water by electron impact as input data. In these studies, water is often used as a model for living matter. Due to the difficulty in accurately describing the ionization of liquid water, we must rely on various approximations. Consequently, most investigations have primarily focused on the vapor phase, thus resulting in a comparatively limited body of research specifically dedicated to liquid water. In general, these investigations indicate the absence of substantial discrepancies in the cross sections corresponding to the liquid and vapor phases of water. This observation



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is particularly unexpected, given the considerable dissimilarities in their inherent physical properties. We theoretically study the single ionization of liquid water by fast electrons using a first-order, independent electron approximation. The initial state of a water molecule in the liquid is described via a Wannier orbital formalism. This technique generates orbitals that are localized on a single molecule and contain information about its interaction with the surrounding liquid medium.

In previous works, we computed multiple differential cross sections for fixed-in-space molecules as well as double differential cross sections (DDCSs) [2] for randomly oriented molecules [2–6]. We also calculated triple differential cross sections (TDCSs) in a coplanar arrangement where the incident, scattered, and ejected electron momenta lie all in the collision plane defined by the incident and scattered directions. Moreover, we studied asymmetric reactions in which a fast and a slow electron are detected in the final channel of the reaction. In the present work, we go a step further by estimating the effects of the Post Collisional Interaction (PCI) effects in the final channel by using adequate Gamow factors.

Now, we compute differential cross sections and estimate values for the total cross sections for liquid water at sufficiently high impact energies. The primary goal is qualitative: to shed light on the previously mentioned findings that give, to date, no considerable differences between the predicted cross sections for liquid and vapor water. Moreover, we submit evidence that the isolated wave functions we use are suitable to describe the condensed phase.

The structure of this paper is as follows: Section 2 provides a concise overview of the theoretical method. Our results are presented and discussed in Section 3, and conclusions are drawn in Section 4. Atomic units are employed throughout, except where explicitly stated otherwise.

2. Theoretical Method

We develop a first order model within the First Born Approximation (FBA) in which we include a Coulomb wavefunction in the final channel to describe the Coulomb interaction of the ionized electron with the residual target in this final channel. In this way, our model is similar to the approximation developed for the gas by Houamer et al. [7] named FBA-CW. It is worthy to mention that our FBA model differs substantially from the so-called Plane Wave Approximation (as it is usually named in the electron impact community) in which the incident, scattered, and ejected electrons are all described by plane waves, i.e., no Coulomb functions are used at all. Our approach employs an independent electron approximation, as described in our earlier publications [2–6]. We also make the assumption that the target relaxation is negligible because the effective collision times are shorter than the relevant relaxation timescales at the incident energies of interest.

The complexity of the multielectronic problem is reduced to a mono-electronic model with a single active electron. This approach has been proven to be effective in previous studies (Ref. [8], reviewed in [9]) and successfully applied to liquid water [2–6,10].

2.1. The Transition Matrix Element

The *prior* version of the transition matrix element for the reaction of interest reads,

$$T_{if}^- = \langle \Psi_f^- | V_i | \psi_i \rangle \quad (1)$$

where ψ_i is the electronic wavefunction in the initial channel and Ψ_f^- is the final electronic wavefunction with correct asymptotic conditions. V_i is the perturbation in the entrance channel.

2.2. Initial Channel Wavefunction

A realistic description of liquid water is one of the main contributions of our work. Instead of using a delocalized wavefunction for the condensed phase, we employ a clever technique to obtain effective localized orbitals on a single water molecule [11,12].

We choose the wavefunction in the initial channel as,

$$\psi_i = \frac{e^{i\mathbf{k}_i \cdot \mathbf{R}}}{(2\pi)^{3/2}} \Phi_i(\mathbf{r}; \alpha, \beta, \gamma) \quad (2)$$

where $\mathbf{R}$ and $\mathbf{r}$ are the position vectors of the incident and active electrons, respectively, with respect to the center of mass of the molecule, and α, β, γ are the Euler angles defining the orientation of a single water molecule.

The incident fast electron is represented by a plane wave with momentum $\mathbf{k}_i$ and the initial bound state of liquid water is denoted by Φ_i .

To describe this bound state of water molecules in the liquid phase, a Wannier orbital formalism is employed. This approach yields effective localized orbitals for individual water molecules, incorporating information about their interactions with the surrounding liquid medium. Consequently, these effective orbitals resemble their gas-phase counterparts and can be used to compute cross sections. However, the C_{2v} symmetry characteristic of the gas-phase orbitals is lost in the condensed phase due to the influence of neighboring molecules.

In the above mentioned method, the electronic state of the water molecule is described by the Kohn–Sham density functional theory, and the molecular orbitals are created from the occupied, extended Kohn–Sham orbitals employing maximally localized Wannier functions. Through a unitary transformation (U), the Kohn–Sham orbitals (ψ_k) are converted into maximally localized Wannier orbitals,

$$\omega_i = \sum_k U_{ik} \psi_k \quad (3)$$

minimizing the spatial spread

$$\Omega = \sum_k [\langle \omega_i | \mathbf{r}^2 | \omega_i \rangle - \langle \omega_i | \mathbf{r} | \omega_i \rangle^2] \quad (4)$$

where the summation is over all occupied Kohn–Sham states.

Unlike Kohn–Sham orbitals ψ_k , which are spread out across the entire system, the Wannier functions ω_i are localized to specific molecules. This provides a picture of the electron distribution that can be interpreted chemically, similar to how Lewis pairs are visualized. For a standard arrangement, each water molecule has four doubly occupied Wannier orbitals: two for the $O-H$ bonds and two for the lone pairs.

Vuilleumier and co-workers [11,12] introduced an intermediate representation where orbitals are localized to a single molecule but delocalized within it, which may be more suitable for condensed molecular systems. This approach creates effective molecular orbitals (Φ_k) by grouping a molecule assigned Wannier orbitals and then diagonalizing the Wannier Hamiltonian within that molecular subspace. As a result, four effective molecular orbitals are generated for each water molecule. These orbitals Φ_k are unambiguously labeled $1A_1$, $1B_2$, $2A_1$, and $1B_1$ (Figure 1), in analogy with those of the gas. The average ionization energies determined by this procedure are 25.66 eV, 13.15 eV, 10.24 eV, and 8.2 eV, respectively. To simulate the liquid phase, we use the CPMD package (version 3.13.2) [13]. In previous works [14–16], this kind of wavefunction was used to study the fragmentation of core ionized water molecules. However, for the present collisional problem we have

considered a larger simulation box to assure that the obtained wavefunctions tend to zero at the simulation walls in order to satisfy the correct asymptotic behaviour of bound states. Therefore, we have employed a cubic cell of 30 atomic units with periodic boundaries, containing 128 water molecules. This configuration corresponds to the experimental density of water at room temperature and our wavefunctions are extracted from an equilibrated configuration at 300 K.

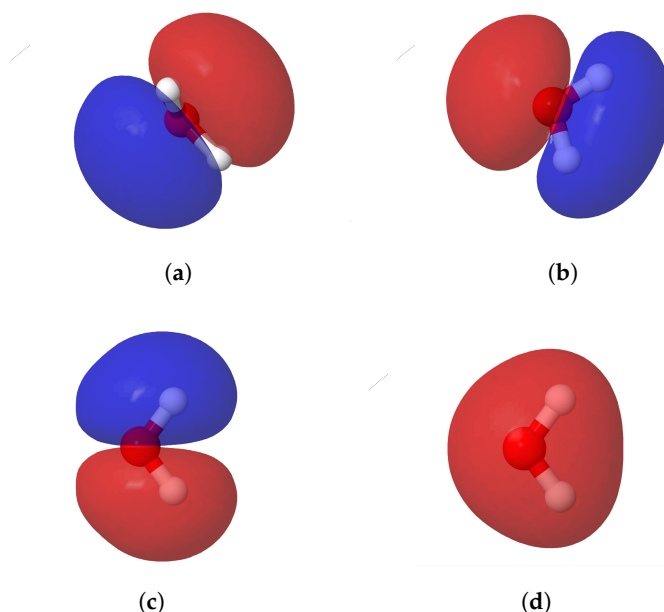


Figure 1. Molecular orbitals for the liquid water (a) $1B_1$, (b) $2A_1$, (c) $1B_2$ and (d) $1A_1$.

The geometry of the water molecule is defined as follows (illustrated in Figure 2): the unit vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ are contained in the molecular plane, pointing along the O–H bond directions, $\mathbf{u}_3$ is a unit vector normal (perpendicular) to this plane and the angle θ is the half-angle between the $\mathbf{u}_1$ and $\mathbf{u}_2$ vectors. For our liquid water, the bond lengths are O–H₁ = 1.94 a.u. and O–H₂ = 1.81 a.u. and the angle is $2\theta = 1.72$ rad. The differences between both bond lengths evidences the lack of C_{2v} symmetry in the liquid.

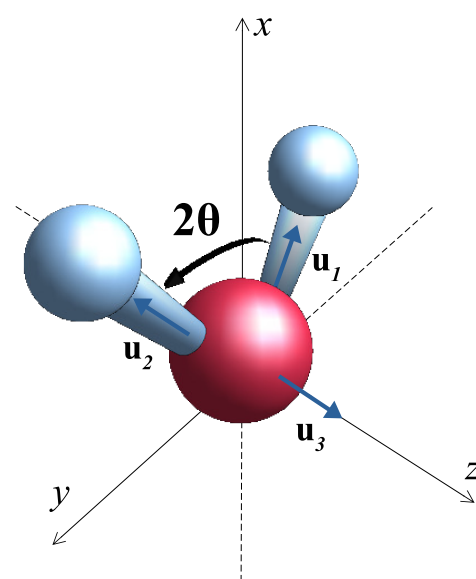


Figure 2. Geometry of the liquid water molecule used in this work (see text).

2.3. Final Channel Wavefunction

The final channel wavefunction is chosen as,

$$\Psi_f^- \cong \frac{e^{i\mathbf{k}_s \cdot \mathbf{R}}}{(2\pi)^{3/2}} C(\mathbf{k}_e, \mathbf{r}, \nu) \quad (5)$$

where $\mathbf{k}_s$ and $\mathbf{k}_e$ are the scattered and ejected electron momenta, respectively, and the continuum Coulomb wave function

$$\begin{aligned} C(\mathbf{k}, \mathbf{r}, \nu) &= \Gamma(1 - i\nu) e^{-\pi\nu/2} \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{(2\pi)^{3/2}} \\ &\times {}_1F_1[i\nu; 1; -i(kr + \mathbf{k} \cdot \mathbf{r})] \end{aligned} \quad (6)$$

describes the ionized electron in the final channel in the field of the residual target at asymptotically large distances, ${}_1F_1$ being the confluent hypergeometric function and $\nu = -Z/k = -1/k$ the corresponding Sommerfeld parameter. The charge $Z = 1$ takes into account the fact that the *passive* electrons produce a complete screening of the nuclear charges of the molecule at asymptotically large distances giving as a result a residual target with a net charge equal to unity. It is worthy to mention that the quantities

$$\Gamma(1 - i\nu) e^{-\pi\nu/2}$$

appearing in Equation (6) lead to the very well known Gamow factor,

$$G(\nu) = |\Gamma(1 - i\nu)|^2 e^{-\pi\nu} = \frac{2\pi\nu}{\exp(2\pi\nu) - 1} \quad (7)$$

that is related to the Coulomb density of states. As we will mention later, this kind of factor is useful to study PCI effects [17–20].

2.4. Perturbation

According to the choice of the initial channel wavefunction given by Equation (2), the perturbation in this channel is,

$$V_i = \frac{1}{|\mathbf{r} - \mathbf{R}|} - \frac{1}{R} = \frac{1}{r_p} - \frac{1}{R} \quad (8)$$

with $r_p = |\mathbf{r} - \mathbf{R}|$. The spatial distribution of the nuclei and *passive* electrons in the water molecule is neglected, obtaining an averaged interaction of the projectile with these particles. Thus, a total screening of the nuclei charge by the *passive* electrons is considered, so the interaction of the projectile with a net charge is equal to unity. The short range part of the real interaction is not taken into account. This approximation has been employed by various authors, including Ref. [21] for gas phase studies and Ref. [10] for liquid phase works.

2.5. Cross Sections

Cross sections are the observables of the reaction. In particular, multiple differential cross sections give detailed information of the reaction as a function of the dynamical and spatial variables of the aggregates of the process under study.

Multiple differential cross sections for ejection of the active electron at a fixed water molecule orientation given by its Euler angles α, β and γ are obtained as,

$$\sigma^{(5)}(\alpha, \beta, \gamma) = N(2\pi)^4 \frac{k_e k_s}{k_i} \left| T_{if}^- \right|^2 \quad (9)$$

where the active electron is ejected with momentum $\mathbf{k}_e$ (and energy E_e) into the differential solid angle Ω_e with respect to the incidence direction (defined by $\mathbf{k}_i$), and the projectile is scattered with momentum $\mathbf{k}_s$ into the solid angle Ω_s . Moreover, as exchange effects are not taken into account, $N = 2$ gives the number of electrons in the initial molecular orbital. Averaging the multiple differential cross sections given by Equation (9) over the Euler angles, we obtain five-fold differential cross sections (5DCS) averaged over all possible molecular orientations,

$$\begin{aligned}\sigma^{(5)} &= \frac{d\sigma}{d\Omega_e d\Omega_s dE_e} \\ &= \frac{1}{8\pi^2} \int \sigma^{(5)}(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma\end{aligned}\quad (10)$$

The double differential cross sections (DDCS) are obtained by the integration of 5DCS over both the scattered solid angle $d\Omega_s$ and the azimuthal angle ϕ_e from $d\Omega_e = \sin\theta_e d\theta_e d\phi_e$

$$\begin{aligned}\sigma^{(2)}(E_e, \theta_e) &= \frac{d\sigma}{d(\cos\theta_e) dE_e} \\ &= \int \sigma^{(5)} d\Omega_s d\phi_e\end{aligned}\quad (11)$$

Single differential cross sections (SDCSs) are obtained by integration of the double differential cross sections over the angle θ_e ,

$$\begin{aligned}\sigma^{(1)}(E_e) &= \frac{d\sigma}{dE_e} \\ &= \int \sigma^{(2)} \sin\theta_e d\theta_e\end{aligned}\quad (12)$$

Finally, total cross sections may be obtained by integrating the SDCS over the ejection energy as given by,

$$\sigma(E_i) = \int_0^{(E_i - I_p)/2} \sigma^{(1)} dE_e \quad (13)$$

where E_i is the impact energy and I_p is the ionization potential of the considered orbital.

To compute the differential cross sections, numerical quadratures are performed within a simulation box.

3. Results

We present triple, double and single differential cross sections and total cross sections for water molecules in the liquid and gaseous phases.

3.1. Triple Differential Cross Sections

Under a coplanar geometry constraint, the 5DCSs (given by Equation (10)) reduce to the so called Triple Differential Cross Sections (TDCSs). Moreover, we consider asymmetric reactions, so exchange effects are disregarded.

In this section, we present TDCS as a function of the ejection angle θ_e for the ionization by fast electron impact of a water molecule.

First, we analyze and give an estimation of the PCI effects in the final channel of the reaction. The use of three Coulomb wave functions in the final channel as in the model by Brauner, Briggs and Klar [22] would be one way. However, the corresponding calculations are very cumbersome and computationally demanding. Moreover, they are out of the scope of this work as our aim is just to give an estimation of the PCI effect. So, we consider

the inclusion of adequate Gamow factors in our TDCS to take into account the Coulomb density of states, as described in Section 2.3. For the repulsive Coulomb interaction between the two outgoing electrons, we use a Gamow factor G_{se} given by:

$$G_{se} = \frac{2\pi/k_{se}}{\exp(2\pi/k_{se}) - 1} \quad (14)$$

where $k_{se} = |\mathbf{k}_s - \mathbf{k}_e|$ is the magnitude of the relative momentum between the scattered and ejected electrons. For the attractive interaction between the scattered electron and the residual target, we use a Gamow factor G_{sT} given by,

$$G_{sT} = \frac{2\pi/k_s}{1 - \exp(-2\pi/k_s)} \quad (15)$$

Figure 3 displays the TDCS for the $1B_1$ orbital at impact energies $E_i = 81$ eV and $E_i = 1$ keV, scattering angle $\theta_s = -10^\circ$ and ejection energy $E_e = 5$ eV. We compare in the figures the effect of the PCI effect at those different impact energies. At $E_i = 81$ eV, the incorporation of PCI effects introduces substantial modifications, resulting in discrepancies of approximately 25% in the recoil region and 60% in the binary region compared to the calculations omitting PCI. Conversely, at $E_i = 1$ keV, these differences are drastically reduced to at most 3% and 6%, respectively. Therefore, in what follows we consider TDCS including the Gamow factors. At variance, we are not taking into account PCI effects in the computation of the double, single and total cross sections at high enough impact energies obtained in this work.

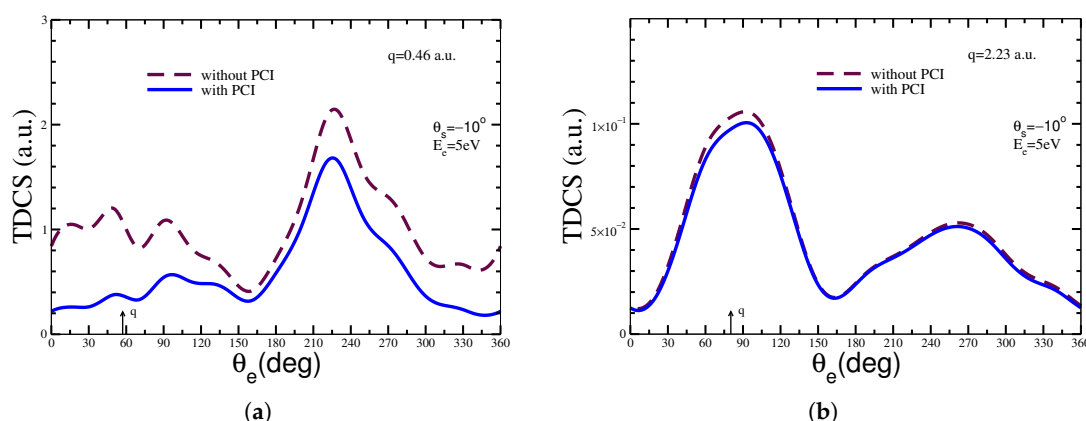


Figure 3. TDCS for ionization from the $1B_1$ orbital as a function of the ejection angle θ_e with (dashed line) and without (solid line) inclusion of the Gamow factors. The impact energies are (a) $E_i = 81$ eV and (b) $E_i = 1$ keV, $\theta_s = -10$ degrees and $E_e = 5$ eV.

In Figure 4, TDCSs for the liquid phase are compared with relative experimental data for the gas phase from Ref. [23] as no experiments are available for the liquid phase. In particular, our TDCS results are multiplied by a factor of 0.6 for optimal visualization. The incident energy is $E_i = 81$ eV, the ejection energies are $E_e = 5$ eV and 10 eV, and the scattering angles are $\theta_s = -6$ and -10 degrees. We also show other theoretical results for gas [19,23,24]: the distorted wave Born approximation (DWBA) from Ref. [23], the Continuum-Distorted-Wave Eikonal-Initial-State (CDW-EIS) model from Ref. [24] and a multicenter-three-distorted-wave (MCTDW) approach from Ref. [19].

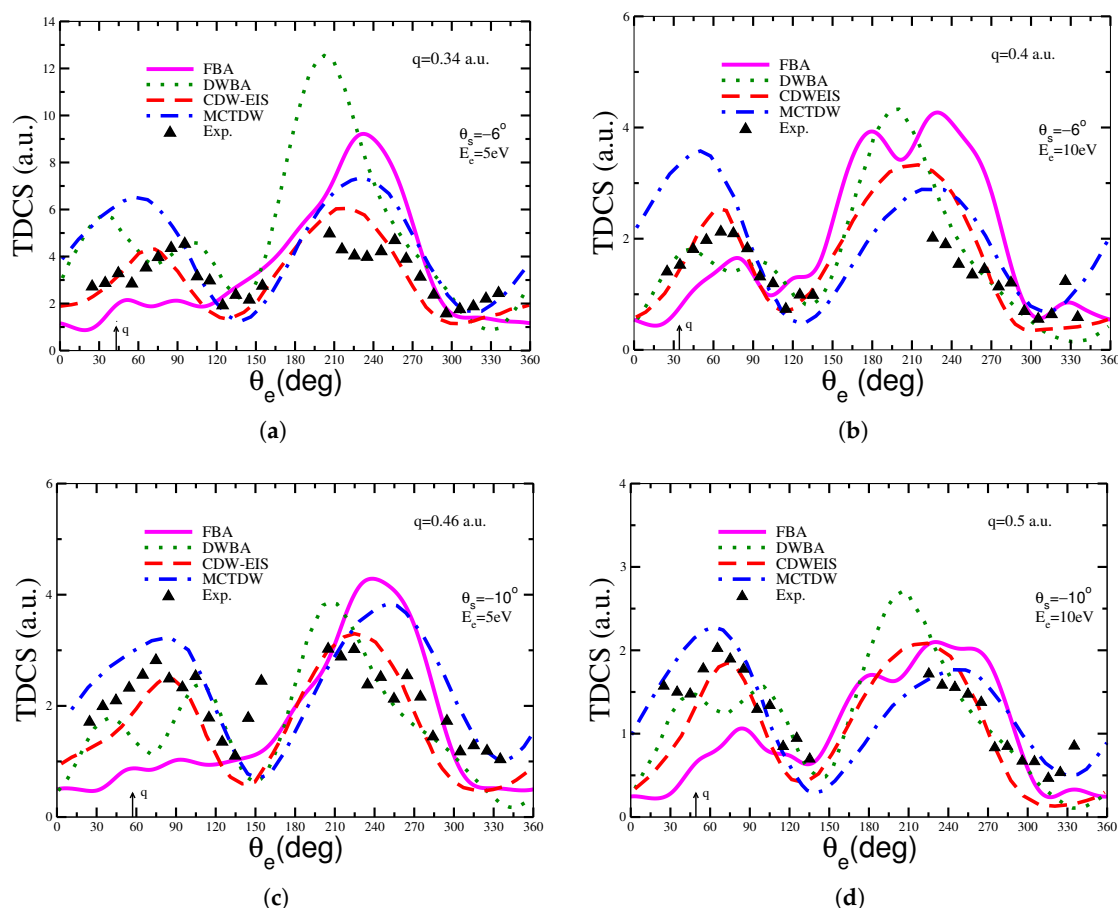


Figure 4. TDCS in a *relative* scale for ionization from the $1B_1$ and $2A_1$ orbitals of liquid water as a function of the ejection angle θ_e . The incident energy is $E_i = 81$ eV and the ejection energies are $E_e = 5$ eV and 10 eV while the scattering angles are $\theta_s = -6$ and -10 degrees. Our results for the liquid FBA with PCI (solid line), experiments from [23] (triangles) and theoretical results DWBA from [23] (dotted line), CDW-EIS from [24] (dashed line) and MCTDW from [19] (dash-dot-dotted line). (a) $\theta_s = -6$ degrees and $E_e = 5$ eV. (b) $\theta_s = -6$ degrees and $E_e = 10$ eV. (c) $\theta_s = -10$ degrees and $E_e = 5$ eV. (d) $\theta_s = -10$ degrees and $E_e = 10$ eV.

We observe a qualitative agreement between our predictions for the liquid phase and those for the gas phase. The results reproduce the structures found in the experimental gas-phase TDCS [23], including peaks in both the binary and recoil regions. At the lowest ejection energy, the ratio between the magnitudes of the maxima in those regions is more significant, with a larger maximum in the recoil region that is consistent with the gas-phase data. The angular position of the transferred momentum $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$ is indicated by an arrow in all TDCS figures.

Regarding the TDCS profiles, the DWBA calculations yield a double-peak binary structure. However, in both sets of experimental data and the other theoretical predictions, the characteristic double-lobe structure of the binary region, typical for p-type orbitals, is absent; instead, a single peak is observed, which is related to how the momentum distribution is sampled under the experimental conditions [18]. In previous calculations, for different energetic conditions corresponding to larger momentum transfer values, we found a double-lobe peak in the binary region. This can be also seen in the studies on gaseous water by Milne-Brownlie et al. [25] ($E_e = 10$ eV, $E_i = 250$ eV and $\theta_s = 10$ degrees, where $q = 1.1$ a.u.), and Kaiser et al. [26] ($E_e = 5$ eV, $\theta_s = 22$ degrees, $E_i = 67.6$ eV and $E_i = 107.6$ eV where $q = 0.77$ a.u. and $q = 0.95$ a.u., respectively).

The theoretical investigations of the gas phase by other authors exhibit significant discrepancies, failing to accurately reproduce experimentally observed features in the TDCS. This has been discussed in previous works of the gas phase [19,23,24]. In contrast to gaseous phase experiments, our liquid-phase results show a decrease in the peak in the binary region with respect to the peak in the recoil region due to the PCI effects. Furthermore, our recoil peak region undergoes a significant broadening.

In Figure 5, we display the discriminated contribution of the two outermost molecular orbitals of liquid water. It can be seen that for these kinematic conditions both the $1B_1$ and $2A_1$ orbitals contribute to the binary and recoil regions to approximately the same extent.

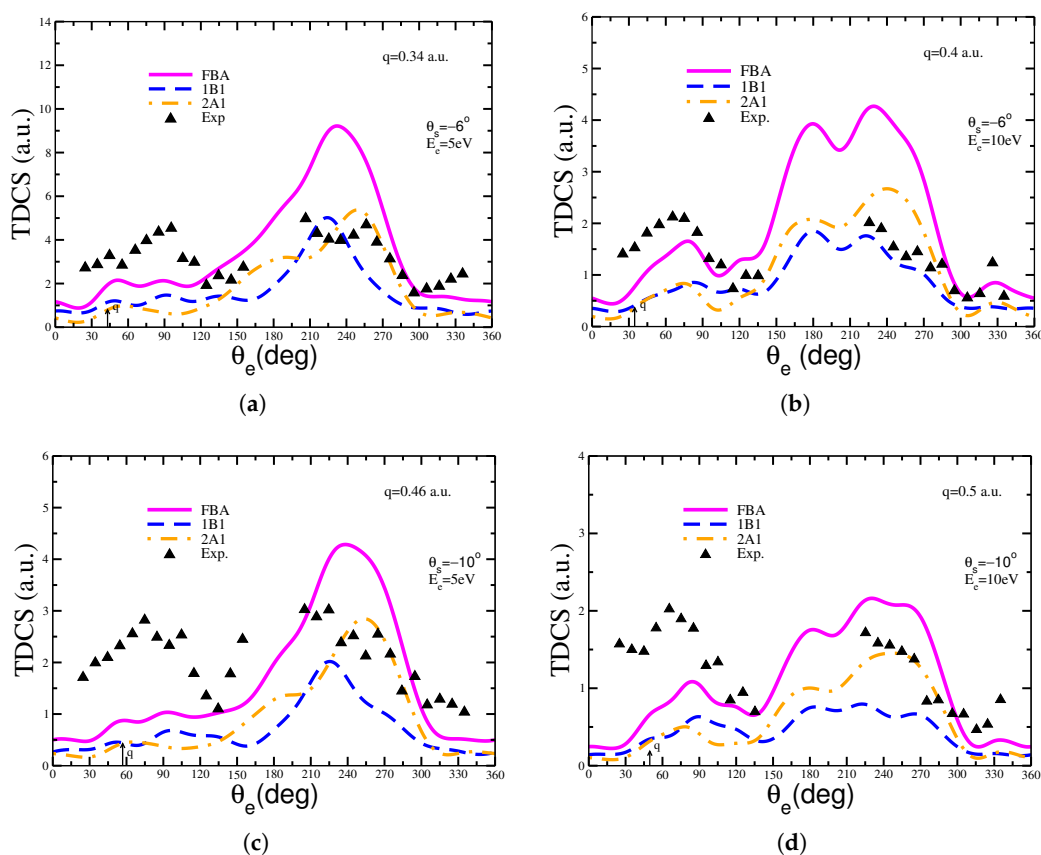


Figure 5. Same kinematic conditions as in Figure 4. For our FBA model with PCI, the discriminated contributions of the orbitals $1B_1$ (dashed line) and $2A_1$ (dash-dotted line), and the sum of both (solid line). (a) $\theta_s = -6$ degrees and $E_e = 5$ eV. (b) $\theta_s = -6$ degrees and $E_e = 10$ eV. (c) $\theta_s = -10$ degrees and $E_e = 5$ eV. (d) $\theta_s = -10$ degrees and $E_e = 10$ eV.

3.2. Double Differential Cross Sections

We present the Double Differential Cross Sections (DDCSs) as a function of the ejection angle θ_e at a fixed incident energy E_i . Due to the lack of experimental DDCS data for liquid water, we compare our results with vapor-phase experiments [27,28] and theoretical models for the gas, including a first-order model with a Coulomb function for the ionized electron (FBA-CW) similar to our model by Houamer et al. [7] and a distorted wave Born approximation (DWBA) calculation of Champion et al. [29,30]. While our calculations show qualitative agreement with existing data, notable differences between gas and liquid phases are evident.

In our early research [2], we compared DDCSs for water in the liquid and gas phases for several molecular orbitals. Our calculations, performed at an incident energy of $E_i = 500$ eV and ejection energies of $E_e = 22$ eV, 40 eV, 64.2 eV, and 100 eV, were in good qualitative agreement with the predictions for the gas [7,29–31], capturing the key physical trends

observed in experiments. Notably, gas-phase predictions and experiments showed a similar peak, albeit at slightly smaller ejection angles.

The trends across both phases were comparable, but quantitative differences were evident. Specifically, the condensed phase Double Differential Cross Sections (DDCSs) were in general higher than the gas ones in almost all the angular domain and ejection energies. Moreover, our DDCSs were generally greater than the experiments for the gas. We identified the evolution of a binary structure that appeared more pronounced at the highest ejection energy.

In Figure 6, an alternative experimental dataset for the gas phase measured at a higher incident energy of $E_i = 1$ KeV is presented. The DDCS changes significantly as the ejection energy varies. At low ejection energies ($E_e = 20$ eV and 40 eV), the DDCSs exhibit a relatively flat maximum around the Bethe region whereas a peak becomes more prominent at higher energies ($E_e = 100$ eV). This peak is associated to binary collision mechanisms, related to classical ionization dynamics. The classical binary peaks for $E_i = 1$ keV are located at a critical angular value, depending on the initial molecular orbital, between 76.6 and 80.2 degrees for 20 eV, 74.7 and 77.3 degrees for 40 eV and, 69.8 and 70.1 degrees for 100 eV. In the sequence of Figure 4a–c, we observe a more rapid evolution to the binary peak for the FBA-CW gas results by Houamer et al. [7] than our liquid results. As explained before, these two approximations are obtained at exactly the same level of theory. Therefore, these discrepancies may be attributed to differences between the gas phase and liquid phase orbitals. Since the momentum distribution of the initial bound state strongly affects the shape of the binary regions in the cross sections, replacing a gas-phase orbital with our effective liquid orbital naturally drives these notable discrepancies against gas data.

In terms of a quantitative analysis, a reversal of the trend previously seen at $E_i = 500$ eV is evident: the DDCSs for the liquid are now consistently lower than those for the gas phase across the entire range of the ejected electron energies. Moreover, the difference between the phases diminishes as E_e increases.

Basically, at low incident energies, the liquid phase exhibits larger DDCSs than the gas phase; conversely, at high incident energies, they are smaller. Furthermore, the DDCS undergoes substantial changes as the energy of the ejected electron varies.

The bottom graphs in Figure 6d–f show the discriminated contributions of each orbital to the DDCS. It can be observed that the contributions of the three outermost orbitals are of the same order of magnitude, whereas the one corresponding to the $1A_1$ orbital is one hundred times smaller (in this figure, multiplied by a factor of 100 for a better visualization). In the binary region, the contributions of the $2A_1$ and $1B_2$ orbitals are more significant than the corresponding $1B_1$ orbital.

3.3. Single Differential Cross Sections

In this section, we present the Single Differential Cross Sections (SDCSs) as a function of the ejection energy E_e as given by Equation (12).

We compare our liquid water calculations with experiments for vapor [27,28], as well as with other theoretical results of first-order models for the gas: a first Born approximation (FBA-CW) [7] and a distorted wave Born approximation (DWBA) [29].

Figure 7 displays the SDCSs at incident energies of $E_i = 500$ eV and 1 KeV. It is observed that the SDCS magnitudes for the liquid phase are lower than those for the gas phase except at the highest ejection energies. According to Ref. [32], this behavior is attributed to the screening effects inherent to the condensed medium. Notably, the discrepancy between phases is more pronounced at $E_i = 1$ KeV.

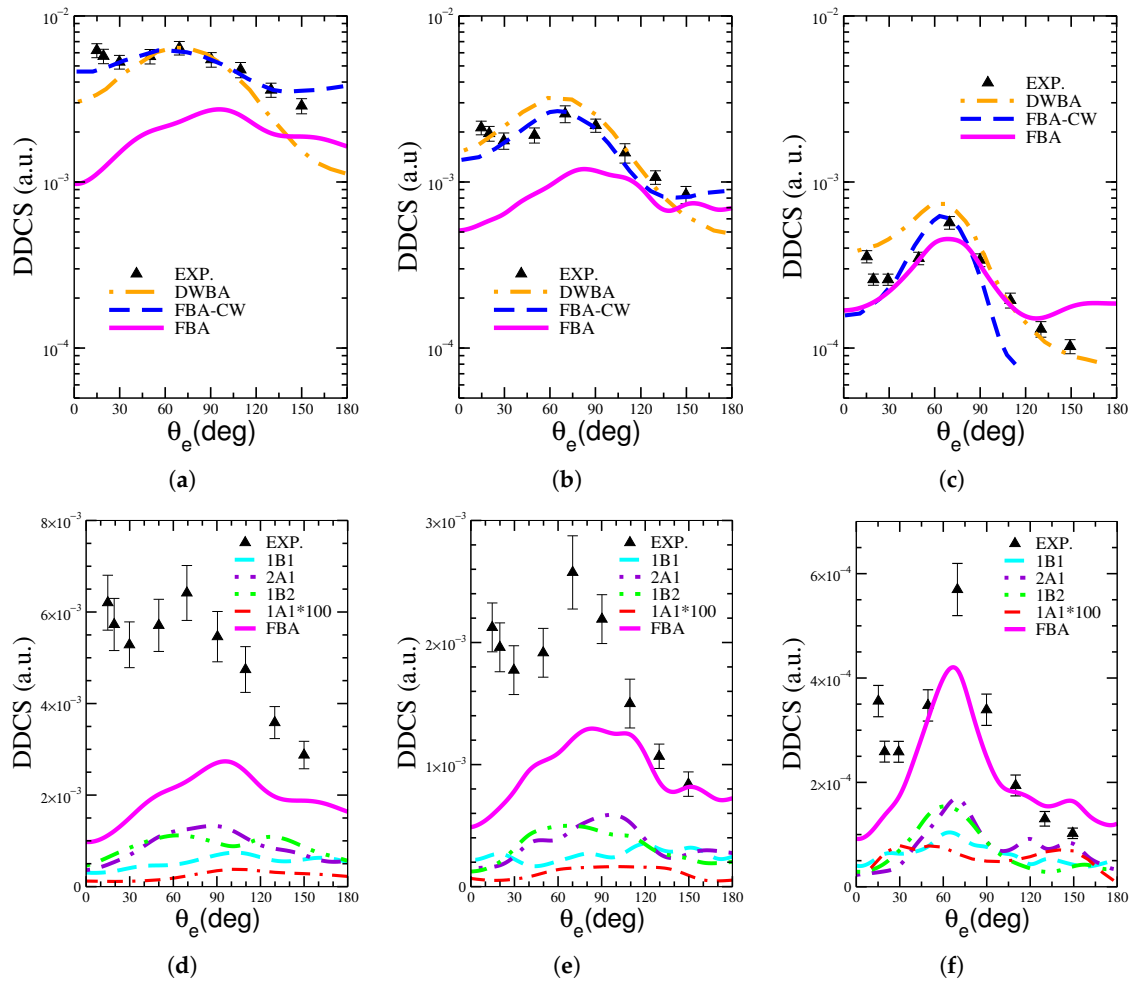


Figure 6. DDCS for the ionization of water molecule at the incident energy of $E_i = 1$ KeV. For (a,d) the ejection energy is $E_e = 20$ eV, (b,e) $E_e = 40$ eV and (c,f) $E_e = 100$ eV. Experiments from [27] (triangles), FBA-CW from [7] (dash line), DWBA from [29] (dash-dotted line) and our FBA for liquid (solid line). (Bottom panel): contributions of each liquid water molecular orbital.

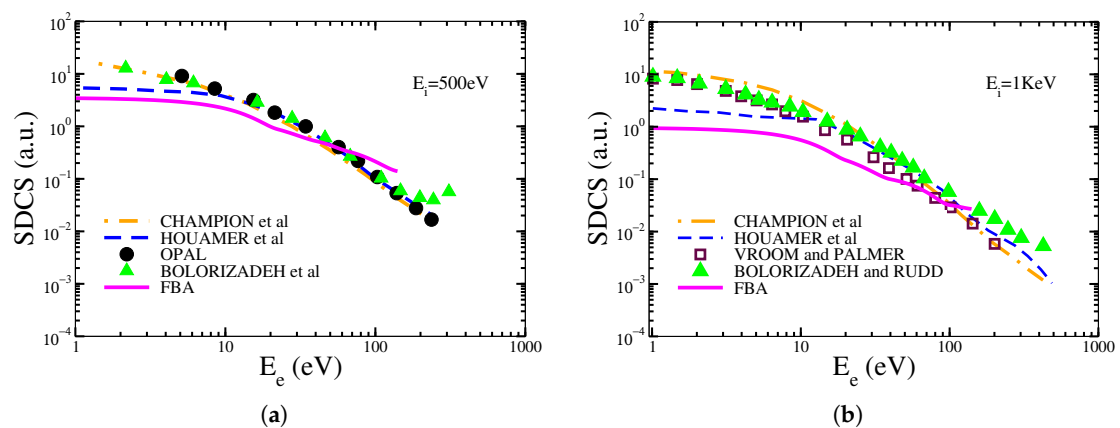


Figure 7. SDCS for ionization of water molecules. The incident energy is (a) $E_i = 500$ eV and (b) 1 KeV. Experiments, from Opal [27] (circles), from Bolorizadeh and Rudd [28] (triangles) and from Vroom and Palmer [33] (square). Theoretical results FBA-CW from [7] (dashed line) and DWBA from [29] (dash-dotted line). Our results FBA for liquid (solid line).

3.4. Total Cross Sections

Integration of the SDCS, as given by Equation (12), over the ejection energy E_e yields to the Total Cross Sections (TCSs) according to Equation (13).

Figure 8 shows TCS as a function of incident energy E_i , including experimental data from Refs. [28,34–38] and theoretical DWBA results from [29]. For comparison, our estimated TCS at incident energies $E_i = 500$ eV and 1 keV are also included.

As expected from the SDCS behavior, our liquid-phase TCS at $E_i = 500$ eV and $E_i = 1$ keV are lower than those for the gas phase. For both phases, all previous TCSs consistently exhibit a broad peak around $E_i \approx 100$ eV. Notably, our liquid-phase results differ significantly from previous experimental and theoretical data for water vapor as can be seen in Figure 8a.

Figure 8b displays the TCS as a function of E_i for various liquid-phase models: a first-order model by Champion [10], simulations by Terrissol [39], and two sets based on the dielectric formalism—one by Dingfelder et al. [40] and another by Nikjoo et al. [41] (based on calculations by Emfietzoglou et al. [42]). As highlighted in Ref. [10], liquid TCS results show notable differences in both their magnitude and the position of the maximum value. However, our results at $E_i = 500$ eV and $E_i = 1$ keV are in good agreement with those by Terrissol [39] and Nikjoo et al. [41] following the same tendency.

TCSs may be employed to obtain other physical magnitudes of interest in fields such as radiobiology, medical physics, etc. One of those magnitudes is the mean free path of the incident particle that can be obtained in a simple way through $\lambda = 1/(n\sigma)$, n in this case being the number of water molecules by volume unit. By using the density of water at normal conditions of pressure and temperature, we obtain that $\lambda(E_i = 500 \text{ eV}) = 2.9$ nm and $\lambda(E_i = 1000 \text{ eV}) = 4.6$ nm. For the sake of comparison, the mean free path reported in Ref. [10] amounts to 3.3 nm and 5.9 nm, respectively. These values could be of interest to determine other magnitudes of relevance in the mentioned fields related to biology.

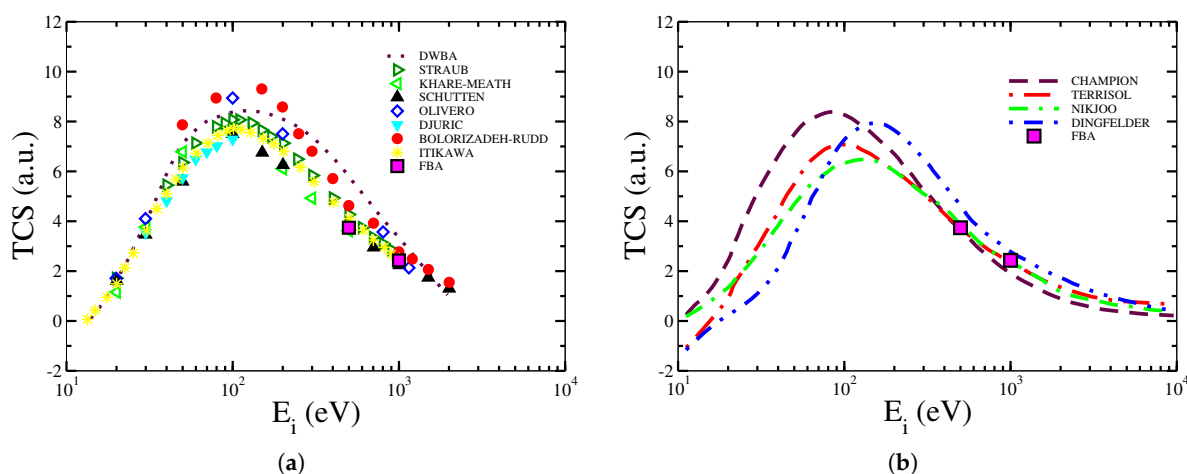


Figure 8. TCS for ionization of water molecules as a function of the incident energy. (a) Comparison with experiments for gas from [34] (triangles right), Ref. [35] (triangles left), Ref. [36] (triangles up), Ref. [37] (diamonds), Ref. [38] (triangles down), Ref. [28] (circles), Ref. [43] (stars) and theoretical results DWBA from [29] (dashed line). (b) Comparison with liquid results from Ref. [10] (dashed line), Ref. [39] (dash-dotted line), Ref. [41] (dash-dot-dotted line), Ref. [42] (dash-dash dotted line).

4. Conclusions

We have studied the single ionization of liquid water by fast electron impact. By means of a Wannier orbital formalism, we obtain a realistic description of molecules in the condensed phase, providing effective orbitals localized on a single molecule. By using a first-order model, we computed triple, double, single differential, and total ionization

cross sections from the most external effective orbitals of a liquid water molecule. The comparison of our results with available measurements and theories for both liquid and gas phases proves evidence that the effective orbitals are reliable in describing the main physical features of ionization reactions of molecules in the condensed phase, such as binary structures observed in the cross sections.

However, we must point out that our model has limitations, as not all the information of the condensed phase is included in the collisional process, such as multiple electron scattering from neighboring molecules, screening beyond static approximation, and energy loss mechanisms in condensed phase.

Moreover, one of the most important findings of our research is that differential and total cross sections for liquid water differ considerably from the experimental and previous theoretical results for water vapor. Although the quantitative capacity of our first order model may be limited at low impact energies, we have shown that our Triple Differential Cross Sections are not greatly modified at high impact energies by inclusion of PCI effects due to the Coulomb interactions between the outgoing electrons and the Coulomb interaction between the scattered electron and the residual target. At variance, inclusion of the Coulomb interaction between the ionized electron and the residual target is crucial to properly describe the ionization reaction by electron impact. Consequently, our qualitative conclusions do not change with inclusion of the mentioned PCI effects in the final channel of the reaction, especially at sufficiently high impact energies. As a fact, we observed a nice agreement among our estimated TCSs and other theories. In this way, liquid water would exhibit a different behaviour in the ionization process with respect to vapor. This conjecture is still a matter for future work. We hope our work promotes future experiments to test our predictions for the liquid phase.

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References

1. Boudaiffa, B.; Cloutier, P.; Hunting, D.; Huels, M.A.; Sanche, L. Resonant Formation of DNA Strand Breaks by Low-Energy Electrons. *Science* **2000**, *287*, 1658–1662. [PubMed]
2. de Sanctis, M.L.; Politis, M.F.; Vuilleumier, R.; Stia, C.R.; Fojón, O.A. Electron emission from water molecules by ion impact: A quantum-classical study. *Eur. Phys. J. D* **2017**, *71*, 125. [CrossRef]
3. Fojón, O.A.; de Sanctis, M.L.; Vuilleumier, R.; Stia, C.R.; Politis, M.F. Ionization of liquid water by fast ion impact. *J. Phys. Conf. Ser.* **2011**, *288*, 012010. [CrossRef]
4. de Sanctis, M.L.; Politis, M.F.; Vuilleumier, R.; Stia, C.R.; Fojón, O.A. Electron emission from water molecules by ion impact. *J. Phys. B At. Mol. Opt. Phys.* **2012**, *45*, 045206. [CrossRef]

5. de Sanctis, M.L.; Politis, M.F.; Vuilleumier, R.; Stia, C.R.; Fojón, O.A. Model potentials in liquid water ionization by fast electron impact. *J. Phys. Conf. Ser.* **2015**, *583*, 012023. [\[CrossRef\]](#)
6. de Sanctis, M.L.; Politis, M.F.; Vuilleumier, R.; Stia, C.R.; Fojón, O.A. A theoretical study of the ionization of water by fast electron impact. *J. Phys. B At. Mol. Opt. Phys.* **2015**, *48*, 0155201. [\[CrossRef\]](#)
7. Houamer, S.; Dal Cappello, C.; Mansouri, A. Differential and total cross sections for the ionization of water molecule by electron impact. *J. Electron. Spectrosc. Relat. Phenom.* **2007**, *161*, 38–40. [\[CrossRef\]](#)
8. Stolterfoht, N.; DuBois, R.D.; Rivarola, R.D. *Electron Emission in Heavy Ion-Atom Collisions*; Ecker, G., Lambropoulos, P., Sobel'man, I.I., Walther, H., Eds.; Springer: Berlin, Germany, 1997.
9. Champion, C.; Lekadir, H.; Galassi, M.E.; Fojón, O.; Rivarola, R.D.; Hanssen, J. Theoretical predictions for ionization cross sections of DNA nucleobases impacted by light ions. *Phys. Med. Biol.* **2010**, *55*, 6053. [\[CrossRef\]](#) [\[PubMed\]](#)
10. Champion, C. Electron impact ionization of liquid and gaseous water: A single-center partial-wave approach. *Phys. Med. Biol.* **2010**, *55*, 11. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Vuilleumier, R.; Sprik, M. Electronic properties of hard and soft ions in solution: Aqueous Na⁺ and Ag⁺ compared. *J. Chem. Phys.* **2001**, *115*, 3454. [\[CrossRef\]](#)
12. Hunt, P.; Sprik, M.; Vuilleumier, R. Thermal versus electronic broadening in the density of states of liquid water. *Chem. Phys. Lett.* **2003**, *376*, 68. [\[CrossRef\]](#)
13. Car, R.; Parrinello, M. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* **1985**, *55*, 2471. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Gaigeot, M.P.; Vuilleumier, R.; Stia, C.; Galassi, M.E.; Rivarola, R.; Gervais, B.; Politis, M.F. A multi-scale ab initio theoretical study of the production of free radicals in swift ion tracks in liquid water. *J. Phys. B At. Mol. Opt. Phys.* **2007**, *40*, 1–12.
15. Tavernelli, I.; Gaigeot, M.P.; Vuilleumier, R.; Stia, C.; Galassi, M.E.; Rivarola, R.; Gervais, B.; Politis, M.F. The Role of the Intermolecular Potential on the Dynamics of Electron Scattering from Water Molecules in Liquid Phase. *ChemPhysChem* **2008**, *9*, 2099–2103. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Stia, C.R.; Gaigeot, M.-P.; Vuilleumier, R.; Fojón, O.A.; Hervé du Penhoat, M.-A.; Politis, M.-F. Theoretical investigation of the ultrafast dissociation of core-ionized water and uracil molecules immersed in liquid water. *Eur. Phys. J. D* **2010**, *60*, 77–83. [\[CrossRef\]](#)
17. Ward, S.J.; Macek, J.H. Wave functions for continuum states of charged fragments. *Phys. Rev. A* **1994**, *49*, 1049. [\[CrossRef\]](#) [\[PubMed\]](#)
18. da Silva, G.B.; Neves, R.F.C.; Chiari, L.; Jones, D.B.; Ali, E.; Madison, D.H.; Ning, C.G.; Nixon, K.L.; Lopes, M.C.A.; Brunger, M.J. Triply differential (e, 2e) studies of phenol. *J. Chem. Phys.* **2014**, *141*, 124307. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Gong, M.; Li, X.; Zhang, S.B.; Niu, S.; Ren, X.; Wang, E.; Dorn, A.; Chen, X. Multicenter three-distorted-wave approach to three-dimensional images for electron-impact-ionization dynamics of molecules: Overall agreement with experiment. *Phys. Rev. A* **2018**, *98*, 042710. [\[CrossRef\]](#)
20. Madison, D.H.; Al-Hagan, O. The distorted-wave born approach for calculating electron-impact ionization of molecules. *J. At. Mol. Opt. Phys.* **2010**, *2010*, 367180. [\[CrossRef\]](#)
21. Champion, C.; Hanssen, J.; Hervieux, P.A. Influence of molecular orientation on the multiple differential cross sections for the (e,2e) process on a water molecule. *Phys. Rev. A* **2001**, *63*, 052720. Erratum in *Phys. Rev. A* **2005**, *72*, 059906.
22. Brauner, M.; Briggs, J.S.; Klar, H. Triply-differential cross sections for ionisation of hydrogen atoms by electrons and positrons. *J. Phys. B At. Mol. Opt. Phys.* **1989**, *22*, 2265–2287. [\[CrossRef\]](#)
23. Ren, X.; Amami, S.; Hossen, K.; Ali, E.; Ning, C.G.; Colgan, J.; Madison, D.; Dorn, A. Electron-impact ionization of H₂O at low projectile energy: Internormalized triple-differential cross sections in three-dimensional kinematics. *Phys. Rev. A* **2017**, *95*, 022701. [\[CrossRef\]](#)
24. Acebal, E.; Otranto, S. Continuum-distorted-wave eikonal-initial-state description of the electron-impact ionization of H₂O at low impact energies. *Phys. Rev. A* **2018**, *98*, 012703. [\[CrossRef\]](#)
25. Milne-Brownlie, D.S.; Cavanagh, S.J.; Lohmann, B.; Champion, C.; Hervieux, P.A.; Hanssen, J. Dynamics in electron-impact ionization of H₂O. *Phys. Rev. A* **2004**, *69*, 032701. [\[CrossRef\]](#)
26. Kaiser, C.; Spieker, D.; Gao, J.; Hussey, M.; Murray, A.; Madison, D.H. Coplanar symmetric and asymmetric electron impact ionization studies from the 1b₁ state of H₂O at low to intermediate impact energies. *J. Phys. B At. Mol. Opt. Phys.* **2007**, *40*, 2563. [\[CrossRef\]](#)
27. Opal, C.B.; Beaty, E.C.; Peterson, W.K. Tables of secondary-electron-production cross sections. *Data* **1972**, *4*, 209. [\[CrossRef\]](#)
28. Bolorizadeh, M.A.; Rudd, M.E. Angular and energy dependence of cross sections for ejection of electrons from water vapor. I. 50–2000-eV electron impact. *Phys. Rev. A* **1986**, *33*, 882. [\[CrossRef\]](#)
29. Champion, C.; Hanssen, J.; Hervieux, P.A.J. Electron impact ionization of water molecule. *Chem. Phys.* **2002**, *117*, 197. [\[CrossRef\]](#)
30. Champion, C.; Hanssen, J.; Hervieux, P.A.J. Differential and total (e,2e) cross sections of simple polyatomic molecules. *Chem. Phys.* **2004**, *121*, 9423. [\[CrossRef\]](#)

31. Long, K.A.; Paretzke, H.G.; Müller-Plathe, F.; Diercksen, G.H.F. Calculation of double differential cross sections for the interaction of electrons with a water molecule, clusters of water molecules, and liquid water. *J. Chem. Phys.* **1989**, *91*, 1569. [[CrossRef](#)]
32. Joshipura, K.N.; Gangopadhyay, S.; Limbachiya, C.G.; Vinodkumar, M. Electron impact ionization of water molecules in ice and liquid phases. *J. Phys. Conf. Ser.* **2007**, *80*, 012008. [[CrossRef](#)]
33. Vroom, D.A.; Palmer, R.L. Measurement of energy distributions of secondary electrons ejected from water vapor by fast electrons. *J. Chem. Phys.* **1977**, *66*, 3720. [[CrossRef](#)]
34. Straub, H.C.; Lindsay, B.G.; Smith, K.A.; Stebbings, R.F. Ionization of H₂O by fast electrons. *J. Chem. Phys.* **1998**, *108*, 109. [[CrossRef](#)]
35. Khare, S.P.; Meath, W.J. Cross sections for the direct and dissociative ionisation of NH₃, H₂O and H₂S by electron impact. *J. Phys. B At. Mol. Phys.* **1987**, *20*, 2101. [[CrossRef](#)]
36. Schutten, J.; de Heer, F.J.; Moustafa, H.R.; Boerboom, A.J.H.; Kistenmaker, J. Gross- and Partial-Ionization Cross Sections for Electrons on Water Vapor in the Energy Range 0.1–20 keV. *J. Chem. Phys.* **1966**, *44*, 3924. [[CrossRef](#)]
37. Olivero, J.J.; Stagat, R.W.; Green, A.E.S. Electron deposition in water vapor with atmospheric applications. *J. Geophys. Res.* **1972**, *77*, 4797–4811. [[CrossRef](#)]
38. Djuric, N.L.; Cadez, I.M.; Kurepa, M.V. H₂O and D₂O total ionization cross sections by electron impact. *Int. J. Mass Spectrom. Ion Process.* **1988**, *83*, R7.
39. Terrissol, M. Modelling of radiation damage by ¹²⁵I on a nucleosome. *Int. J. Radiat. Biol.* **1994**, *66*, 447–451. [[CrossRef](#)] [[PubMed](#)]
40. Dingfelder, M.; Travia, A.; McLawhorn, R.A.; Shinpaugh, J.L.; Toburen, L.H. Electron emission from foils and biological materials after proton impact. *Radiat. Phys. Chem.* **2008**, *77*, 1213–1217. [[CrossRef](#)]
41. Nikjoo, H.; Emfietzoglou, D.; Watanabe, R.; Uehara, S. Can Monte Carlo track structure codes reveal reaction mechanism in DNA damage and improve radiation therapy? *Radiat. Phys. Chem.* **2008**, *77*, 1270–1279. [[CrossRef](#)]
42. Emfietzoglou, D.; Nikjoo, H. The effect of model approximations on single-collision distributions of low-energy electrons in liquid water. *Radiat. Res.* **2005**, *163*, 98–111. [[CrossRef](#)] [[PubMed](#)]
43. Itikawa, Y.; Mason, N.J. Cross Sections for Electron Collisions with Water Molecules. *J. Phys. Chem. Ref. Data* **2005**, *34*, 1. [[CrossRef](#)]

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