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Double differential cross sections for liquid water ionization by fast electron impact

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Abstract. In this work we study theoretically the single ionization of liquid water by impact of energetic electrons. A realistic description of the wavefunction for an isolated water molecule in the liquid phase is made by means of a Wannier orbital formalism. We develop a first order model within the framework of an independent electron approximation in which the relaxation of the target is not taken into account. The double differential cross sections are computed and compared with experimental data and theoretical calculations for gas phase.

1 Introduction

Ionization of water molecules is an important reaction in many domains, such as, plasma physics, fusion experiments, astrophysics, and even in the study of ionizing collisions on living matter. Moreover, secondary electrons produced during the ionization are of the great importance in biological radiation applications, as they play a crucial role in the mechanisms that lead to cell alteration [1]. So, the effectiveness of the radiations is closely related to the angular and energy distributions of this secondary electrons. Track structure analysis based on computer simulations requires as input data, the cross sections for the interactions of electrons with molecules in the living matter which is mainly composed of molecules of water in the liquid phase. However, to obtain an appropriate description for ionization of liquid water is a difficult task. So, several approximations are required to describe the reaction. While most of previous studies have been devoted to isolated water molecules as targets [2–21], only a few ones were recently addressed to the study of the water in the liquid state [21–31].

We study theoretically the single ionization of liquid water by impact of fast electrons with a first-order model obtained in the framework of the independent electron approximation. We describe the initial bound states of the water molecule in the liquid phase through a Wannier orbital formalism by which orbitals located on a single water molecule are at hand [32,33] containing information of the interaction with the rest of the molecules of the liquid medium. In this way, orbitals similar to the gas phase are obtained and can be managed to compute cross sections. However, the C_{2v} symmetry properties of the gas phase orbitals are lost as in the condensed phase the surrounding molecules affect the symmetry of a given single molecule. In previous works, we computed multiple differential cross sections for fixed-in-space molecules as well as for randomly oriented molecules [29–31]. Now, we focus on the double differential cross sections (DDCS) averaged on the molecule orientations and scattering angles in a coplanar geometry. In this coplanar arrangement, the incident, scattered and ejected electron momenta lie all in the collision plane defined by the incident and scattered directions. Moreover, we consider asymmetric reactions in which a fast and a slow electrons are detected in the final channel of the reaction.

Atomic units are used otherwise stated.

2 Theory

Our model (see previous works [29–31] for more details) is based on an independent electron approximation. Besides, we disregard the relaxation of the target as the effective collision times are smaller than the relaxation ones at the considered incident energies. As we suppose asymmetric reactions, the exchange effects may be neglected.

The eight-fold differential cross sections (8DCS) for the single ionization of a fixed-in-space liquid water molecule

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are obtained as,

$$\sigma^{(8)} = \frac{d\sigma}{d\Omega_{mol}d\Omega_e d\Omega_s dE_e}$$
$$= N(2\pi)^4 \frac{k_e k_s}{k_i} \left| \left\langle \Psi_f^- \mid V_i \mid \psi_i \right\rangle \right|^2 \qquad (1)$$

where $\mathbf{k}_i$, $\mathbf{k}_s$ and $\mathbf{k}_e$ are the incident, scattered and ejected electron momenta, respectively. Moreover, $d\Omega_s$ and $d\Omega_e$ denote the solid angles corresponding to $\mathbf{k}_s$ and $\mathbf{k}_e$, respectively. The quantity $d\Omega_{mol} = \sin\beta \, d\alpha \, d\beta \, d\gamma$ being α, β, γ the Euler angles of the water molecule. As exchange is not taken into account, $N = 2$ gives the number of electrons in the considered molecular orbital.

The initial-state wavefunction is chosen as,

$$\psi_i = \frac{e^{i\mathbf{k}_i \cdot \mathbf{R}}}{(2\pi)^{3/2}} \Phi_i(\mathbf{r}) \qquad (2)$$

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.

The incident electron is described by a plane wave while Φ_i represents the initial molecular orbital of liquid water. This phase is simulated with a box of approximately 30 a.u. at 300 K with periodic boundary conditions containing 128 molecules of water. The molecular orbitals are constructed from the occupied extended (Kohn-Sham) ones using the maximally localized Wannier functions. While the Kohn-Sham orbitals are delocalized over the whole system, losing thus the molecular picture, the Wannier functions are local to specific molecules in the liquid. An intermediate representation in which the orbitals are local to a molecule but delocalized within it has been introduced by Vuilleumier and Sprik [33], being perhaps more appropriate for the study of condensed molecular systems [32]. This procedure (see previous works [30,31] for more details and references therein) gives four effective molecular orbitals $1B_1$, $2A_1$, $1B_2$ and $1A_1$ with the average ionization energies 8.26 eV, 10.24 eV, 13.15 eV, 25.66 eV, respectively. The first calculated ionization energy is slightly lower than the reported values for liquid both experimental (9.3 eV [34]) and theoretical (9.1 eV [22]). On the other hand, an accepted first ionization energy for the gas phase is 12.6 eV [9].

The final-state wavefunction is chosen as,

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

as we deal with asymmetric collisions the fast scattered electron is represented by the plane wave while the ionized electron is given by the Coulomb wave

$$C(\mathbf{k}, \mathbf{r}, \nu) = \Gamma(1 - i\nu) \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{(2\pi)^{3/2}}$$
$$\times e^{-\pi\nu/2} {}_1F_1[i\nu; 1; -i(kr + \mathbf{k} \cdot \mathbf{r})] \qquad (4)$$

which describes this particle in the field of the residual target at asymptotically large distances, being ${}_1F_1$

the confluent hypergeometric function and $\nu = -Z^*/k = -1/k$ the corresponding Sommerfeld parameter. The asymptotic charge $Z^* = 1$ corresponds to a total screening of the nuclei charge of the molecule by the passive electrons (not ionized), yielding a residual target with a net charge equal to unity.

The perturbation in the initial channel is taken as,

$$V_i = \frac{1}{|\mathbf{r} - \mathbf{R}|} + V(\mathbf{R}) \qquad (5)$$

where we consider $V(\mathbf{R}) = -1/R$ that corresponds to a complete screening of the nuclear charges by the passive electrons [30,31,35] that besides it does not take into account their spacial distributions.

Integrating the 8DCS given by equation (1) over the Euler angles, we obtain five-fold differential cross sections (5DCS) averaged over all possible molecular orientations,

$$\sigma^{(5)} = \frac{d\sigma}{d\Omega_e d\Omega_s dE_e}$$
$$= \frac{1}{8\pi^2} \int \sigma^{(8)}(\alpha, \beta, \gamma) \sin\beta \, d\alpha \, d\beta \, d\gamma. \qquad (6)$$

Finally, we obtain double differential cross sections (DDCS) by integrating 5DCS over both the scattered solid angle $d\Omega_s$ and the azimutal angle ϕ_e of the $\mathbf{k}_e$ where $d\Omega_e = \sin\theta_e d\theta_e d\phi_e$

$$\sigma^{(2)}(E_e, \theta_e) = \frac{d\sigma}{d(\cos\theta_e)dE_e}$$
$$= \int \sigma^{(5)} d\Omega_s d\phi_e. \qquad (7)$$

3 Results

We compute DDCS for ionization of a liquid water molecule as a function of the ejection angle for a fixed incident energy E_i. As no measured DDCS for liquid water are available, we compare our DDCS with experiments for vapor [2,4] as well as calculations for this phase of a first order model (denoted FBA-CW) [36] that is similar to ours, where the projectile and ejected electron are also described by a plane and a coulomb wave, respectively, but the molecular orbitals are those of Moccia [37] for the gas. We also include calculations with the distorted wave Born approximation (DWBA) from references [38,39] and other results obtained in the framework of the density functional theory (DFT) from reference [40]. In general, a good qualitative agreement is found but significant differences between gas and liquid are observed.

In previous works [30,31] we compared our results for 5DCS for several orbitals of the liquid water molecule with the ones of the gaseous phase. A good qualitative agreement was obtained, we could reproduce the main physical features of the 5DCS, i.e., the binary and recoil peaks. In order to validate further our model, we go a step ahead and focus on the DDCS. To contrast with available experimental and theoretical data, we calculate DDCS for an incident energy $E_i = 500$ eV as a function of the ejected electron angle and fixed ejection energies E_e of 22 eV, 40 eV,
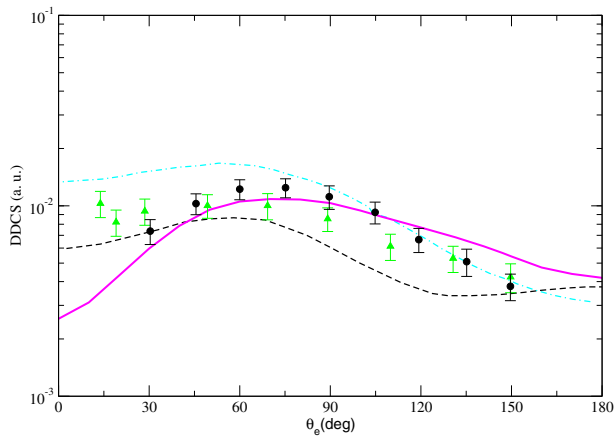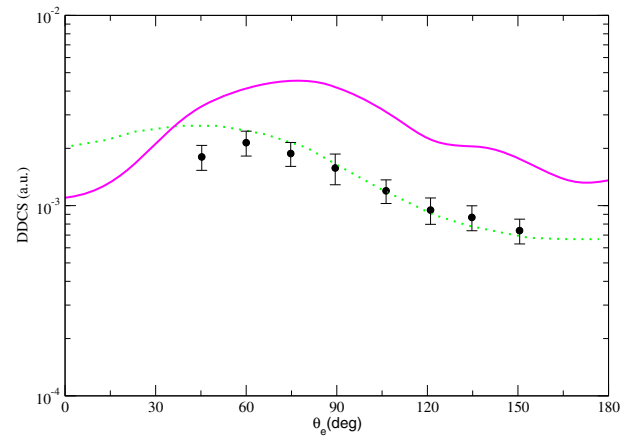
Fig. 1. DDCS for ionization of water molecules as a function of the ejection angle θ_e. Incident and ejection energies are $E_i = 500$ eV and $E_e = 22$ eV, respectively. For liquid, full line: our results. For gas, dashed line: FBA-CW calculations [36], dashed-and-dotted line: DWBA calculations [38], circles: experiments by Opal et al. [2], triangles: experiments by Bolorizadeh and Rudd [4].
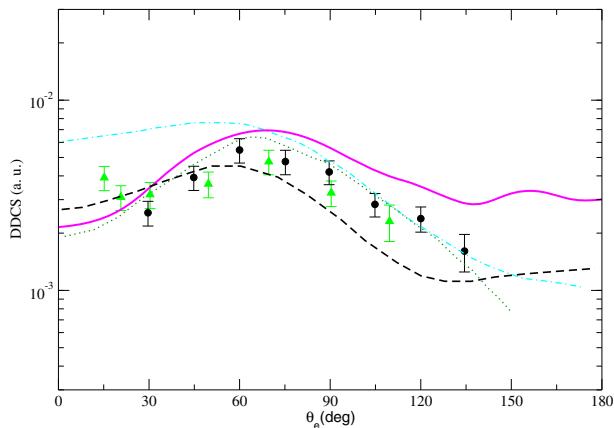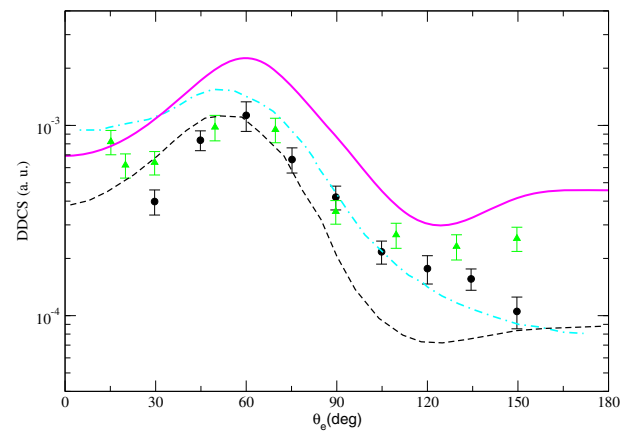

Fig. 2. Same as Figure 1 but $E_e = 40$ eV. Dotted line: DFT calculations from reference [40].

Fig. 3. Same as Figure 1 but $E_e = 64.2$ eV. Dotted line: DWBA calculations for gas from reference [39].

Fig. 4. Same as Figure 1 but $E_e = 100$ eV.

64.2 eV and 100 eV. They are shown in Figures 1–4, respectively. We find a good qualitative agreement between our predictions and the ones of the gas [36,38–40]. As the ejection energy increases, the DDCS evolves from a rather flat distribution at $E_e = 22$ eV to a situation in which a peak is observed at about $\theta_e = 70°$ at $E_e = 40$ eV and ending with a prominent peak structure located about $\theta_e = 60°$ for $E_e = 100$ eV. This peak may be associated to the binary classical mechanisms for ionization coming from each orbital. Predictions and experiments for the gas phase exhibit this binary peak at slightly lower ejection angles. In terms of the magnitude of the cross sections, the first order models give differences between the phases, being our DDCS for liquid higher than the corresponding to the gas in almost all the angular domain for the ejection energies E_e of 22 eV, 40 eV and 100 eV (there are no FBA-CW data for $E_e = 64.2$ eV). Additionally, our DDCS overestimate the experiments for the gas except

for the lowest ejection energy $E_e = 22$ eV at small angles. In general, a similar behavior is seen with the different theoretical data. We observe for the DDCS the general same trend as in the 5DCS, i.e., the DDCS cross secction for the liquid phase result in general higher than those for the gaseous phase at sufficiently high ejection energy. As a matter of fact, at $E_e = 100$ eV our predictions for DDCS are higher than all the ones reported in the other theoretical and experimental works [36,38–40]. However, at lower ejection energies such as $E_e = 22$ eV our DDCS are smaller than other computed DDCS and experiments for ejection angles below 30°. This differences at low energies and ejection angles may have an influence in the single differential cross sections integrated over all ejection angles and, consequently, on the total cross sections as a function of the incident energy. Evaluation of these cross section is in progress.

4 Conclusions

We study the single ionization of liquid water molecules by the impact of rapid electrons by using a first order model in a framework of an independent electron

approximation [30,31]. This model has a proper characterization of the condensed phase since the bound states of a single water molecule in the liquid are obtained as expansions of the maximum localized Wannier functions [32,33]. We present DDCS as a function of the ejection angle at fixed incident energy for several ejection energies. As no measurements for liquid water are available at present, we contrast our predictions with reported theoretical and experimental results for the gas phase. The physics underlying in the ionization reaction in the liquid phase evidenced by the presence of the binary peaks in the DDCS is almost the same as in the gas phase although quantitative differences are observed. In general, DDCS for the condensed phase are higher than the ones of the gas at high enough ejection energies. However, the situation is reversed for slow secondary electron at small ejection angles. This finding may have an importance in the corresponding integrated cross sections (whose computation is in progress at present). Moreover, this could be important to fully understand the interaction of the ionizing radiations with the biological tissue as the slow secondary electrons may play a relevant role in the energy deposition processes leading to cell damage.

Author contribution statement

All authors contributed equally to the paper.

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