Ionization of liquid water by fast electron impact: multiple differential cross sections for the 1B\(_1\) orbital

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Abstract. We present a theoretical study of single ionization of water molecules in liquid phase by impact of fast electrons in a coplanar geometry. Multiple differential cross sections are obtained through a first order model obtained within the framework of an independent electron approximation in which relaxation of the target is not taken into account. The wavefunctions for a single water molecule in the liquid phase are obtained through a Wannier orbital formalism and the ejected electron is described by means of Coulomb functions. We also present averaged calculations over all molecular orientations. A comparison with previous theoretical and experimental results, the latter corresponding to water in gas phase, shows a good agreement. The main physical features of the reaction (such as binary and recoil peaks) present in measurements for vapor are also observed in the present theoretical predictions.

1. Introduction

Ionization of water molecules in liquid phase is of relevance in several domains such as radiobiology and medical physics. As the biological matter is composed mainly of water, the analysis of this reaction is crucial to understand the damage provoked to the living tissue by the ionizing radiations. In particular, the production of low energy secondary electrons resulting from a primary ionization reaction of water is of importance to elucidate the mechanisms that lead to cell alteration. In track structure analysis, the liquid water molecules in living cells are treated often as gas water molecules to simplify the study. So, a more realistic description is required. Moreover, recent studies on (e, 2e) processes with liquid phase [1, 2] show little differences with the gas one in spite of the fact that they have very different physical properties. This needs an explanation. Therefore, we initiate the study of the single ionization of water molecules in liquid phase by fast electron impact, i.e., impact energies of some hundreds of eV.

The ionization by electron impact of water in gas phase has been studied since long time ago ([3], [4], see [5] for a review). On the contrary, only a few works deal with the liquid phase [1, 2]. In order to treat properly this phase, one has to describe in a realistic way the electronic states of the molecules. This is a difficult task that taken in conjunction with those of the collision itself (among them the correct description of the Coulomb interactions between charged fragments in the final channel of the reaction) turns the problem practically irresoluble. Therefore, several approximations are required in order to obtain the observables of the reaction.
Our aim is to study in a simple manner the dynamics involved in the \((e,2e)\) reaction with water in the liquid phase. We present a simple first-order model developed within the framework of an independent electron approximation that constitutes the departure point for more elaborated ones. Thus, we employ an independent electron approximation in which the passive electrons of the molecule (those not ionized during the collision) remain as frozen in their initial orbitals. In this way, the multielectronic problem is reduced to a monoelectronic one. This approximation was used in many works dealing with multielectronic targets ([6], [7], see also [8] for a review) and even for liquid water [2]. In these works, it is assumed that the effective collision time at high impact energies is much smaller than the relaxation time. In analogous way and for the sake of simplicity, we assume that this condition is valid.

We compute MDCS for the \(1B_1\) orbital of the water molecule as a function of the ejection angle at definite scattering angle, incident and ejected energies, and for fixed orientations of the molecule. In particular, we consider coplanar geometries in which the incident, scattered and ejected electrons lie in the same plane. Moreover, we analyze asymmetric kinematic conditions for the scattered and ejected electrons (ejected energies of some eV). To circumvent the challenges presented by the description of the liquid phase, we employ an interesting Wannier orbital formalism that transforms the wavefunction of the whole liquid system into electronic orbitals localized over each water molecule in the liquid phase [9]. As experimental results of MDCS at fixed molecular orientations for liquid water are not available, we compare our theoretical predictions with other theoretical ones obtained for the gas phase [10]. In addition, as molecules are randomly oriented in experiments with water vapor [11], we also present molecular cross sections averaged over all the molecular orientations.

As is well known, electronic emission is most probable in the direction given by the momentum transfer that may be obtained by conservation laws from the projectile electron-active electron subsystem. Consequently, this fact may be ascribed to a binary collision between the two mentioned particles. This classical ionization mechanism may be traced in the quantum MDCS by the presence of a prominent peak, the so called binary peak being one of the most important physical features of the MDCS. It is worthy to mention that the presence of the peak is verified in the case of active electrons coming from initial \(s\) orbitals whereas for those coming from \(p\) ones, the binary peak may be split up into two lobes symmetric with respect to the direction of the momentum transfer. Another important physical characteristic of the MDCS is the so called recoil peak observed in measurements at almost the opposite direction at which appears the binary peak. This may be related to a two-step mechanism in which the active electron suffers a binary collision with the projectile and then the electron is back scattered elastically by the target nucleus. This gives rise to another peak in the MDCS, in general less prominent than the binary peak that can be thus associated to this mechanism in two steps. The presence of these characteristic peaks will be studied in the liquid phase.

Atomic units are used except otherwise explicitly stated.

2. Theory

In the framework of an independent electron model, we develop a simple monoelectronic approximation considering that the passive electrons of the reaction (electrons of the target that are not ionized) remain as frozen during the reaction in their initial orbitals. In this way, MDCS for the active electron (the one to be ionized) for a coplanar geometry at a fixed molecule orientation defined by de Euler angles are obtained as,

\[
\sigma^{(8)}(\alpha, \beta, \gamma) = \frac{d\sigma}{d\Omega_{\text{mol}} d\Omega_v d\Omega_e dE_e} = N(2\pi)^{-1} \left| \frac{k_k k_e}{k_i} \langle \Psi^- | V_i | \psi_1 \rangle \right|^2
\]
where $\psi_i$ and $\Psi_f^-$ are the initial and the final wavefunctions (the latter with correct boundary conditions), respectively, and $V_i$ is the perturbation in the initial channel. $k_i, k_s$ and $k_e$ are the incident, scattered and ejected electron momenta, respectively, and $E_e$ is the ejected electron energy. $d\Omega_i$ and $d\Omega_s$ denote the solid angles corresponding to $k_e$ and $k_s$, respectively, whereas $d\Omega_{\text{mol}} = \sin \beta \, d\alpha \, d\beta \, d\gamma$ where $\alpha, \beta, \gamma$ are 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 wavefunction is chosen as,

$$\psi_i = \frac{e^{ik_eR}}{(2\pi)^{3/2}} \Phi_i(r)$$  \hspace{1cm} (2)

where $R$ and $r$ are the position vectors of the incident and active electron, respectively, with respect to the center of mass of the molecule. A plane wave describes the incident electron and $\Phi_i$ represents the initial molecular orbital of the water molecule in the liquid phase. Briefly, this phase is simulated with a box of approximately 30 a.u. at 300K with periodic boundary conditions containing 128 molecules of water. The water orbitals are constructed from the occupied extended (Kohn-Sham) ones using the maximally localized Wannier functions. In this way, effective molecular orbitals localized on single molecules are obtained [9]. Band positions are related to average orbital energies. This procedure gives for the 1B$_1$ orbital for the liquid phase an average ionization energy equal to 8.2 eV.

The final wavefunction is chosen as,

$$\Psi_f^- \equiv \frac{e^{ik_eR}}{(2\pi)^{3/2}} C(k_e, r, \nu)$$  \hspace{1cm} (3)

where the continuum Coulomb wave function

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

describes the ionized electron in the final channel at asymptotically large distances, being $\Gamma$ the confluent hypergeometric function and $\nu = -Z^*/k_e = -1/k_e$ 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.

The perturbation in the entrance channel $V_i$ is given by

$$V_i = \frac{1}{|r - R|} - \frac{1}{R}$$  \hspace{1cm} (5)

in accordance with the choice of the initial wavefunction and with the following approximation. We neglect the spatial distribution of the nuclei and passive electrons in the water molecule, obtaining an average for the interaction of the projectile with these particles. Thus, we consider the interaction of the projectile with a net charge equal to unity that is equivalent to consider a total screening of the charge of the nuclei by the passive electrons at all distances. So, the short range part of the real interaction is neglected. This approximation was used by several authors, see for instance [6] for the gas and [2] for the liquid phase.

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

$$\sigma^{(5)} = \frac{1}{8\pi^2} \int \sigma^{(8)}(\alpha, \beta, \gamma) \sin \beta \, d\alpha \, d\beta \, d\gamma$$  \hspace{1cm} (6)

To compute the cross sections, numerical quadratures are performed within the simulation box.
Figure 1. Perpendicular orientation of the water molecules considered in Fig. 2

Figure 2. MDCS per electron for perpendicular orientation of the water molecules as in Fig. 1 for an incident energy $E_i = 250$ eV, ejected energy $E_e = 5$ eV and scattering angle $\theta_s = 15^\circ$. Full line, present results. Dashed line, gaz phase results [10]. Binary and recoil peak angles are indicated by arrows (see text)

3. Results
We present coplanar geometry results of MDCS for the ionization of the 1B$_1$ orbital of liquid water. We consider first an incident energy $E_i = 250$ eV, ejected energy $E_e = 5$ eV and scattering angle $\theta_s = 15^\circ$. As experimental results of MDCS at fixed molecular orientations for liquid phase are not available, we compare our theoretical predictions with other theoretical ones obtained for water molecules in gaz phase [10]. These previous calculations correspond also to a first order model in which the water orbitals in gaz phase are obtained through a development centered on the heavy oxygen atom as given by Moccia [12]. We consider the case of molecules oriented with its molecular plane perpendicular to the collision one being the latter defined by the incident and scattering directions (see figure 1). In order to make the comparison possible, we present results in which the part 1/R of the perturbation is not taken into account in our calculations as the previous theoretical calculations [10] do not include this term. However, as will be seen below,
Figure 3. Summed experimental MDCS on a arbitrary scale for the 1b$_1$ and 3a$_1$ orbitals of randomly oriented water molecules in gaz phase for an incident energy $E_i = 250$ eV, ejected energy $E_e = 10$ eV and scattering angle $\theta_s = 15^\circ$ extracted from Ref. [11]. Binary and recoil peak angles for the 1b$_1$ orbital are indicated by arrows.

this term is of relevance to properly represent the physical features of the reaction observed in measurements. In Fig. 2, it can be seen that our predictions agree well in a qualitative way with the ones corresponding to the gaz phase. In particular, both predictions are of the same order. Results for the gaz phase exhibit a deep minimum around $\theta_e = 210^\circ$ that also appears for the liquid phase although in a less pronounced way. The theoretical results predict a binary peak two-lobe structure at the expected classical angular value of about $\theta_q = 76.5^\circ$ and $\theta_{-q} = 75.7^\circ$ for the liquid and the gaz phases, respectively. This values are indicated in the figure but they are almost undistinguishable. The $\theta_{-q}$ recoil angular position is also shown. The 1B$_1$ orbital has a strong $p$ character and accordingly to this, a two-lobe structure is observed in the binary peak region.

In Fig. 3, we show the experimental results on a relative scale for the gaz phase corresponding to the sum of the independent 1b$_1$ and 3a$_1$ orbital contributions as the experiments are not able to resolve their difference in energy especially in the recoil region. It can be seen that experiments show the main physical features associated to the ionization reaction, i.e., the binary and the recoil peaks.

In Fig. 4 we present our results of MDCS averaged over all molecular orientations for the 1B$_1$ orbital for an incident energy $E_i = 250$ eV, ejected energy $E_e = 10$ eV and scattering angle $\theta_s = 15^\circ$. Normalized experiments for vapor from [11] corresponding only to the 1b$_1$ orbital are shown. As mentioned above, the experimental resolution of the measurements is not able to resolve the contributions from the 1b$_1$ and 3a$_1$ orbitals in the recoil peak region, so experimental results belonging only to the binary region are presented in Fig. 4. It can be seen that our results present a good qualitative agreement with the experiments in the binary region describing the characteristic two-lobe structure of a $p$ orbital. Moreover, our results are also in qualitative good agreement with a previous first-order calculations for water in gaz phase [13]. In this calculation the initial state is represented as in Ref. [10] by using a plane wave for the incident electron and the Moccia’s molecular wavefunction for the bound state of the target in the gaz phase. The final state is described as the product of a plane wave for the scattered electron and a Coulomb wave function with effective ionic charge $Z^* = 1$ (1CW model) for the
Figure 4. MDCS averaged over all molecular orientations for an incident energy $E_i = 250$ eV, ejected energy $E_e = 10$ eV and scattering angle $\theta_s = 15^\circ$. Experiments for the gas phase are extracted from Ref. [11] and normalized conveniently. Full line, present results for the liquid phase. Dashed line, 1CW model for the gas phase [13]. Dotted line, FBA-CW for liquid phase [2]. Dash-dotted line, FBA-CW for the gas phase [2]. Binary and recoil peak angles for the $1B_1$ orbital are indicated by arrows.

We have studied ionization of water molecules in the liquid phase by means of simple first order model by using an independent electron approximation. The wave function of a single ionized electron. In addition, the $1/R$ term is included in the perturbation. This model uses the independent electron approach to reduce the multielectronic problem to a monoelectronic one by neglecting the relaxation of the target. We also show in the figure the results for the gas and liquid phase obtained with a single-center partial-wave approach [2]. In this model (FBA-CW), water molecules in both thermodinamical phases are described by means of single-center molecular wavefunctions developed in a Gaussian basis. It is worthy to mention that this model and the 1CW one are similar to ours except in the description of the bound state. Although molecules in the liquid phase do not exhibit the same symmetries as in the gas phase, the $1B_1$ orbital used in this work is almost symmetric. Therefore, the MDCS to first order present also an almost symmetric curve with respect to the momentum transfer direction as in the case of molecules in the gas phase. All the theoretical predictions present binary and recoil structures in qualitative good agreement. However, it is surprising that the results for the gas and liquid phase given by the FBA-CW model are practically the same. On the contrary, quantitative differences are observed between our results and the ones corresponding to the gas phase given by the 1CW and FBA-CW models. For instance, the height of the lobes in the binary region given by the 1CW model is almost 50% lower than the one of our results for liquid whereas the situation is reversed for the recoil peak. At last, there is a very good agreement between our predictions and the ones of the FBA-CW approximation. In fact, only slight differences are seen in the magnitude of the two-lobe structure and the recoil region. In general, results for the liquid phase in the binary region are higher than the ones for the gas indicating that the $1B_1$ orbital is more diffuse in the liquid phase leading to greater cross sections. This fact is attributed in [2] to polarization effects provoked by the surrounding molecules.

4. Conclusions
We have studied ionization of water molecules in the liquid phase by means of simple first order model by using an independent electron approximation. The wave function of a single
molecule in the liquid phase has been obtained through the use of Wannier orbitals techniques [9]. The results obtained so far show that the main physical features observed in experiments for vapor (such as binary and recoil peaks) are similar to the ones observed in our results. Moreover, a very good qualitative agreement with previous result for the liquid is found. These findings are encouraging to extend our work to the other orbitals of liquid water. This task is in progress and once finished may be useful to understand the basics of the dynamics involved in the reaction of interest. If the trend for MDCS for the other orbitals is similar to the one for the $1B^1$ orbital, then we will be in position to improve the approximations used in our simple model. For instance, we assume that the relaxation of the target is negligible during the collision time as was assumed previously for reactions with molecules in both phases. However, we cannot establish at this very first stage of our studies if this condition really holds for the liquid as experiments for this phase are not available. A more detailed study on this point is out of the scope of the present work. Previous results for the gaz and liquid phase obtained with a single-center partial-wave approach [2] are practically the same. This is surprising taking into account the important differences in the physical properties between both thermodinamical phases. Although our results for the liquid are in qualitative agreement with previous predictions for the gaz, some quantitative differences are observed. However, it is not possible to determine to what extent these differences will remain for the integrated MDCS. All the subjects pointed out here will be matter of analysis in future works.

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References
[1] Haïed H, Eschenbrenner A, Champion C, Ruiz-López R F, Dal Cappello C, Charpentier I, Hervieux P -A 2007 Chem. Phys. Lett. 439 55.
[2] Champion C 2010 Phys. Med. Biol. 55 11.
[3] Opal C B, Beaty E C, Peterson W K 1972 At. Data 4 209.
[4] Straub H C et al 1996 Phys. Rev. A 54 2146.
[5] Itikawa Y, Mason N J 2005 J. Phys. Chem. Ref. Data 34 1.
[6] Dal Cappello C, Hervieux P A, Charpentier I, Ruiz-Lopez F 2008 Phys. Rev. A 78 042702.
[7] Champion C, Lekadir H, Galassi M E, Fojon O, Rivarola R D and Hanssen J, 2010 Phys. Med. Biol. 55 6053.
[8] Stolterforht N, DuBois R D and Rivarola R D 1997 Electron Emission in Heavy Ion-Atom Collisions ed G Ecker, P Lambropoulos, I I Sobelman and H Walther (Berlin: Springer)
[9] Hunt P, M. Sprik and R. Vuilleumier 2003 Chem. Phys. Lett. 376 68.
[10] Champion C et al 2001 Phys. Rev. A 63 052720; Champion C. et al 2005 Phys. Rev. A 72 059906.
[11] Milne-Brownlie D. S. et al 2004 Phys. Rev. A 69 032701.
[12] Moccia R 1964 J. Chem. Phys. 40 2186.
[13] Champion C, Dal Cappello C, Houamer S and Mansouri A 2006 Phys Rev. A 73 012717.