Model potentials in liquid water ionization by fast electron impact

M L de Sanctis\textsuperscript{1}, M-F Politis\textsuperscript{2}, R Vuilleumier\textsuperscript{3}, C R Stia\textsuperscript{1} and O A Fojón\textsuperscript{1}

\textsuperscript{1}Instituto de Física Rosario (CONICET-UNR), Av. Pellegrini 250, 2000 Rosario, Argentina.
\textsuperscript{2}LAMBE, CNRS UMR 8587, Université d’Evry Val d’Essonne, Boulevard François Mitterrand, 91025 Evry, France.
\textsuperscript{3}École Normale Supérieure, Dépt. de Chimie, UMR 8640 CNRS-ENS-UPMC, 24, rue Lhomond, 75005 Paris, France.

E-mail: mdesanctis@ifir-conicet.gov.ar

Abstract. We study the ionization of water molecules in liquid phase by fast electron impact. We use our previous first-order model within an independent electron approximation that allows the reduction of the multielectronic problem into a monoelectronic one. The initial molecular states of the liquid water are represented in a realistic way through a Wannier orbital formalism. We complete our previous study by taking into account approximately the influence of the passive electrons of the target by means of different model potentials. We compute multiple differential cross sections for the most external orbital $1B_1$ and compare them with other results.

1. Introduction

The ionization of water molecules by electron impact plays an important role in several domains such as radiobiology, radioprotection and medical physics. In fact, this basic reaction is crucial to understand the damage provoked to living tissue by the ionizing radiations. In particular, the production of low energy electrons is of importance to elucidate the mechanisms that lead to cell alteration [1]. In track structure analysis, the liquid water molecules in living cells are often treated as if they were in the gas phase. So, a realistic description of the reaction for molecules in the liquid phase is required to deeply understand the mechanisms in which they are involved. However, a proper description of molecules in the liquid phase is a difficult task that added to the complexities of the collision dynamics makes the problem practically intractable. Hence, several approximations are required in order to obtain the observables of the reaction, i.e., the cross sections.

In a recent work [2], we developed a simple monoelectronic first-order model within the framework of an independent electron approximation to compute multiple differential cross sections (MDCS) for the ionization of the most external $1B_1$ liquid water orbital by fast electron impact. We assume that one of the target electrons (the active one) is ejected in the final channel whereas the other ones (the passive electrons) remain as frozen in their initial states. In this way, the many electron problem is reduced to a monoelectronic one. The orbitals of a single molecule in the liquid phase are represented through a Wannier orbital formalism [3]. The model predicts the presence in the MDCS of the well known binary and recoil peaks similar to the ones of the gas phase [4, 5]. Unfortunately, MDCS for the liquid phase are not available...
at present. Here, we extend our previous work [2] by considering the influence of the passive electrons on the MDCS by means of model potentials in the entrance channel of the reaction.

Atomic units are used otherwise stated.

2. Theory

As in Ref. [2], the eight-fold differential cross sections (8DCS) for the single ionization of a fixed-in-space liquid water molecule are obtained as,

$$
\sigma^{(8)} = \frac{d\sigma}{d\Omega_{\text{mol}}d\Omega_{\text{e}}d\Omega_{\text{s}}dE_{e}} = N(2\pi)^4 \frac{k_{i}k_{s}}{k_{i}} \left| \langle \Psi_{f}^{-} \mid V \mid \psi_{i} \rangle \right|^2
$$

where \(k_{i}, k_{s}\) and \(k_{e}\) are the incident, scattered and ejected electron momenta, respectively. Moreover, \(d\Omega_{s}\) and \(d\Omega_{e}\) denote the solid angles corresponding to \(k_{s}\) and \(k_{e}\), respectively. \(d\Omega_{\text{mol}} = \sin \beta \, d\alpha \, d\beta \, d\gamma\) being \(\alpha, \beta, \gamma\) 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 and final-state wavefunctions are chosen as,

$$
\psi_{i} = \frac{e^{ik_{i} \cdot R}}{(2\pi)^{3/2}} \Phi_{i}(r) \quad \Psi_{f}^{-} \approx \frac{e^{ik_{e} \cdot R}}{(2\pi)^{3/2}} C(k_{e}, r, \nu)
$$

respectively, where \(R\) and \(r\) are the position vectors of the incident and active electrons, respectively, with respect to the center of mass of the molecule. \(\Phi_{i}\) represents the initial molecular orbital of liquid water obtained through a Wannier orbital formalism [3] and the incident electron is described by a plane wave. In the final channel, the ionized electron is described by the Coulomb wavefunction \(C(k, r, \nu) = \Gamma(1-i\nu) (2\pi)^{-3/2} e^{ikr} e^{-\nu \pi/2} F_{1}[i\nu; 1; -(kr + k_{i}r)]\) where \(F_{1}\) is the confluent hypergeometric function, and \(\nu = -1/k\) is the Sommerfeld parameter.

The perturbation in the initial channel is taken as,

$$
V_{i} = \frac{1}{|r - R|} + V(R)
$$

where \(V(R)\) is a model potential for the projectile-target interaction. We consider no relaxation of the residual target during the reaction. By neglecting the spatial distribution of the nuclei and passive electrons in the water molecule, we obtain an average for the interaction of the projectile with these particles. Firstly, we consider \(V(R) = -1/R\) that corresponds to a complete screening of the net nuclear charge by the passive electrons [2]. In this way, the short range part of the real interaction is neglected. Secondly, to take into account in a simple way the repulsion between the active electron and the passive ones, we include a short range potential given by,

$$
V_{\text{short}}(R) = -\sum_{j} N_{j} \frac{1}{R} \exp(-2Z_{j}^{eff}R) \left(1 + Z_{j}^{eff}R\right)
$$

where \(Z_{j}^{eff}\) is an effective atomic charge and summation runs over all orbitals \(j\). Here, both Belkić [6] and Slater [7] charges are considered. The corresponding model potentials \(V(R)\) are denoted as \(V_{B}\) and \(V_{S}\), respectively. Furthermore, we test a first order of a Green-Sellin-Zachor type model potential given by \(V_{G} = -\frac{1}{R} - \frac{Z^{2}}{3R^{2}} e^{-R/d} - \frac{Z}{R} (H-1)(Z-1) e^{-2R/d}\), where \(d, H\) and \(Z\) are taken as the ones for the Ne [8] that is isoelectronic to water. Finally, we employ the model potential \(V_{i} = -\frac{8-N}{R} - N e^{-2\alpha R} - Ne^{-2\alpha R}\) with the \(N\) and \(\alpha\) parameter values given in Ref.[9].

Integrating the 8DCS given by Eq. (1) over the Euler angles, five-fold differential cross sections (5DCS) averaged over all possible molecular orientations, are obtained.
3. Results

We compute multiple differential cross sections for single ionization of liquid water molecules from the most external 1B\textsubscript{1} orbital. Asymmetric kinematic conditions for both scattered and ejected electrons (ejection energies of some eV) are considered. The collision takes place in a coplanar geometry in which the incident, scattered and ejected momenta lie all in the same plane.

First, we present 8DCS for fixed-in-space water molecules as a function of the ejection angle $\theta_e$. Two particular arrangements where the molecule is oriented perpendicularly to the collision plane are considered (see Fig. 1).

![Fixed-in-space molecule configurations considered in this work. Unit vectors $u_1$ and $u_2$ define the molecular plane. (a) Normal I orientation. (b) Normal II orientation.](image)

In Fig. 2, we present results for an incident energy $E_i = 250$ eV, ejected energy $E_e = 5$ eV and scattering angle $\theta_s = 15^\circ$. In this case, the momentum transfer is $q = 1.1$ a.u. and the ionization process is expected to exhibit the typical features of a binary collision regime. This is the case for the Normal I orientation (Fig. 2(a)) where the 1B\textsubscript{1} orbital is directed along the incidence direction. The 8DCS computed with $V(R) = -1/R$ show the characteristic $p$-orbital two-lobe structure appearing at around the binary peak region ($\theta_e \approx 75^\circ$). On the contrary, for the Normal II orientation (Fig. 2(a)) the orbital is oriented perpendicularly to the incidence direction favouring ejection at $\theta_e = 90^\circ$ and $\theta_e = 270^\circ$. The overall behavior observed for both orientations can be explained by the strong $p$-character of the 1B\textsubscript{1} orbital and the interplay between both terms of the perturbation given by Eq. (3).

Calculations for the different model potentials are also included in Fig. 2. Slight differences between 8DCS obtained with a Slater potential $V_S$ and the ones for the $-1/R$ contribution are found. It can be seen that the $V_S$ potential preserves the general trend of the angular distribution. On the contrary, for the model potentials $V_B$, $V_G$ and $V_I$, strong deviations are observed for both configurations. In particular, for the Normal I (Fig. 2(a)) orientation the two-lobe structure is practically erased.

![8DCS per electron for the 1B\textsubscript{1} orbital as a function of the ejection angle for $E_i = 250$ eV, $E_e = 5$ eV, and $\theta_s = 15^\circ$. (a) Normal I and (b) Normal II orientations.](image)
Second, in Fig. 3, 5DCS are presented for the cases of $V(R) = -1/R$ and $V(R) = V_S$ and compare with experiments for the gas [4]. The incident and ejected energies are $E_i = 250$ eV and $E_e = 10$ eV, respectively, whereas $\theta_s = 15^\circ$. Experimental and theoretical results present the same shape at the binary region. In general, qualitative agreement is observed between liquid and gas phases calculations [10, 11]. Moreover, very good accord is observed between our calculations and the previous ones for the liquid [11] obtained also through a first order approximation and a Gaussian monocentric expansion for the water orbitals. Finally, the inclusion of the model potential $V_S$ in our perturbation provokes enhanced cross sections at the recoil region.

4. Conclusions
We have studied the ionization from water molecules in the liquid phase by means of our previous first-order model based on an independent electron approximation [2]. The wavefunction of a single molecule was obtained through the use of Wannier orbitals techniques [3]. The main physical features observed in experiments for vapor (such as binary and recoil peaks) are similar to the ones observed in our predictions (see also Ref.[2]). Moreover, there is a very good agreement with previous predictions for liquid water. From our present results, we estimate that the passive electrons of the reaction may play a role in the recoil region. In particular, the Slater model potential $V_S$ seems to be more suitable to describe the cross sections. It would be interesting to check if this behavior is verified for the other orbitals of the liquid water. Work in this direction is in progress.

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