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DOUBLE IONIZATION OF H_2O MOLECULE BY ELECTRON IMPACT

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Abstract

We present the five fold differential cross section (FDCS) and the four fold differential cross section (FourDCS) for electron impact double ionization of the water molecule, for all the molecular orbitals of the target. A theoretical approach called FBA-CW based on the first Born approximation where the projectile is represented by a plane wave, while Coulomb wave functions are used to describe the ejected electrons, taking into account their interaction with the residual ion. Because there are no calculations and no experimental data to compare with our results, the model is applied for two series of experimental conditions which could be used in a next future. Recently, it has been shown that experimental and theoretical data about the ionization of biological systems were needed in fundamental studies of charged particle interaction in biological material, which is commonly modeled by water.

Keywords *: "Double ionization", "H_2O molecule", "Five fold cross section", "Electron impact*".

I - INTRODUCTION

The study of collision between charged particles and molecules is of great and fundamental importance in several fields of applied physics. Such a process is fundamental to the understanding of the role of electron-electron correlation and the electronic structure of the target.

This process represents an interesting tool, for the study of the ionization mechanism itself, in astrophysics and plasmas physics [1], and even in the effect of radiation damage on living matter [2]. As water is a ubiquitous liquid with particularly interesting properties, especially because it constitutes 80% of the biological systems, it has attracted major interest in experimental and theoretical researches. Today it is recognized that when water is irradiated and ionized the ejected electrons can have enough kinetic energies to ionize other molecules. These fast reactions lead to the formation of stable molecules (such as H_2 and O_2) and free radicals (H^+, OH^-). However results of this primary and secondary species are in reality products of the destruction of water molecules surrounding DNA [2]. For this interest and particularity of water molecule target, many theoretical [3] and experimental [4-7] investigations were performed in the case of the single ionisation. The most extensive experiment was realised by Opal et al [5] where they measured the doubly differential cross section DDCS at an incident energy of 500 eV.

Several groups have also measured partial cross section [8-11] with different degrees of precision, nevertheless the total SI cross section is not effected by these differences since the H^+ contribution is greatest compared to that of OH^- and H_2^+ [8-9]. Model calculations such as the Binary-Encounter-Dipole (BED) model [10] are shown to provide remarkable methods to predict differential and total ionization cross section [11-12]. The role of molecule orientation on the collision process was studied [13] where authors confirmed the necessity to take into account the particular molecular orientation when the ionization cross section of polyatomic molecules is calculated. Results of this method were then compared with corresponding measurements [14].

We find in literature only few experiments dedicated for this molecule. The case of the triply differential cross section (TDCS) is the more dramatic as in our knowledge only the measurements of Milne-Brownlie et al.[14] are currently available. For the other multiply differential cross sections, we can cite the extensive work performed by Opal et. al. [16] in which doubly and single differential cross sections were provided for an incident energy of 500 eV in the ejection energy range 4-205 eV and at ejection angles $\theta_e = 30° - 180°$, and the works of Bolorizadeh and Rudd [17] and of Oda [18] at the incident energy of 500 eV. The literature is however more abundant for singly differential cross section (SDCS) and total cross section (TCS) [19-25]. On the theoretical side, earlier calculations largely limited to plane wave Born approximation (PWBA) showed only qualitative agreements with experiments [26-28]. The semi empirical (BEB) calculations give on the other hand better agreement with experiments [29]. Very recently, Champion et al. have applied the distorted wave Born approximation (DWBA) to evaluate multiply and total cross sections for water molecule [30] and extended the method for simple polyatomic molecules [31].The results were found to be in fair agreement with experiments except in the case of the TDCS where recoil peaks have not been reproduced [14].

Now, the differential and total cross section for the nondissociative and dissociative single ionization of water are well established, however the investigation of multiple ionization of H_2O induced by electron impact is rather poor. This process would be understand and should be taken in account to describe the interaction electron-matter.

In 1995 U. Werner and co workers [32] have reported for the first time the investigation of multiple ionization and fragmentation of water by proton impact of 100-400 eV using a position and time sensitive multi-particles detector. Then F. Fremont et al [33] analyzed the different fragments produced by the single double and triple ionization of H_2O by 16-200 eV incident electrons. More recently the valence and double ionization of small water clusters (Water molecule, water dimmer and the cyclic water cluster $(H_2O)_3$ and $(H_2O)_4$ were calculated [34] by Green's propagator method which allow for the direct computation of ionization energies by searching the poles of an approximation to the Green's function. The corresponding pole strengths are related to spectral intensities, which are a measure for the intensities in experimental spectrum. The pole and pole strengths of the approximated Green's function are derived by solving an eigenvalue problem [34] and the conclusion was that the double ionization spectra of the water clusters are very rich in structures and phenomena, each spectrum contains spectra of different origin.

As water is a very interesting target, there is a great interest in the cross section of electron impact single and double ionization of water for use in charged particles track structure analysis, and in modelling radiation damage in biological samples.
To this end we reserve this work to calculate the five fold differential cross section for the so-called (e-3e) reaction on the water molecule by incident electron energy of 1000eV, using the first Born approximation. The initial state is described by a product of a plane wave (for the incident electron) and molecular H_2O wave function; the latter is a linear combination of atomic orbital (LCAO), all centred on the heavy oxygen atom (self consistent field LCAO molecular orbital, developed by Moccia 1964) [35]. In the exit channel the ejected electrons are represented by two coulomb wave functions, whereas the scattered electron is described by a plane wave function. A Gamow factor is introduced here to involve the repulsion between the two lowest electrons. Moreover we do not consider the exchange effects in the FDCS calculation because of the large asymmetry of the collision energies (the ejected energies are smaller if compared to the scattered one). This method was successfully used in the case of the double ionization of different target He [36] and H_2 [37].

The paper is organized as follows: Section II outlines the theory used to describe the process. In section III, our results are presented. Finally, a conclusion is given in section IV.

II - THEORY

We study the reaction:

$$e^- + H_2O \rightarrow 3e^- + residual \text{ target} \tag{1}$$

and consider the dissociative double ionisation of the triatomic system from its ground by fast electron impact. We will suppose that the internuclear distance is at its equilibrium value and that the collision time is much smaller than the period of all other processes such as rotation and vibration (see for instance Wightman et al 1993[36]).
The exchange effects are neglected because the scattered electron is faster than the ejected one in all cases considered here.
In a perturbative treatment of the Born approximation the five-fold differential cross section (FDCS) is written as:

$$\frac{d^5\sigma}{d\Omega_a d\Omega_b d\Omega_s dE_a dE_b} = \sigma^{(5)} = \frac{k_a k_b k_s}{k_i} \left| f_{B1} + f_{B2} \right|^2 \tag{2}$$

where $d\Omega_s$, $d\Omega_a$ and $d\Omega_b$ denote, respectively, the elements of solid angle for the scattered and the two ejected electrons. f_{B1} and f_{B2} are the first and the second terms of the Born series. The energy intervals of the two ejected electrons are represented by dE_a and dE_b. In our study, we shall use only the first born approximation:

$$f_{B1} = \frac{-1}{2\pi}\left\langle \psi_f(\vec{r}_1, \vec{r}_2, \vec{k}_a, \vec{k}_b)e^{i\vec{k}_s.\vec{r}_0}\left|V(r_0, r_1, r_2, R)\right|e^{i\vec{k}_i.\vec{r}_0}\psi_i(\vec{r}_1, \vec{r}_2)\right\rangle \tag{3}$$

With :

$$V(r_0, r_1, r_2) = -\frac{1}{r_0} + \frac{1}{\left|\vec{r}_0 - \vec{r}_1\right|} + \frac{1}{\left|\vec{r}_0 - \vec{r}_2\right|} \tag{4}$$

and :

$$\psi_f(\vec{r}_1, \vec{r}_2, \vec{k}_a, \vec{k}_b) = \left(\frac{\varphi_c(\vec{k}_a, \vec{r}_1)\varphi_c(\vec{k}_b, \vec{r}_2) + \varphi_c(\vec{k}_a, \vec{r}_2)\varphi_c(\vec{k}_b, \vec{r}_1)}{\sqrt{2}}\right)\varphi(\left|\vec{k}_a - \vec{k}_b\right|) \tag{5}$$

with:

$$\varphi_c(\vec{k}_e, \vec{r}) = \frac{\exp(i\vec{k}_e.\vec{r})}{(2\pi)^{3/2}}\exp\left(\frac{\pi Z}{2k_e}\right)\Gamma(1 + iZ/k_e)\,{}_1F_1\left(-iZ/k_e, 1, -i(k_e r + \vec{k}_e.\vec{r})\right) \tag{6}$$

r_0 is the distance between the incident electron and the center of the molecule, r_1 and r_2 the distance between one electron and Z=2. In reality the ejected electrons feel a three-center Coulomb potential and equation (6) is an approximation.

The term $\varphi(\left|\vec{k}_a - \vec{k}_b\right|)$ is the repulsive Gamow factor:

$$\varphi(\left|\vec{k}_a - \vec{k}_b\right|) = \exp(-\pi\chi_{ab}/2)\Gamma(1 - i\chi_{ab}) \tag{7}$$

And

$$\chi_{ab} = \frac{1}{\left|\vec{k}_a - \vec{k}_b\right|} \tag{8}$$

II.1 - The Target Wawe Function

For all the considered molecules, the ground state of the bound electrons with the position vectors $\vec{r}_1$, $\vec{r}_2 \ldots \vec{r}_n$ is described by one-center wave functions given by Moccia [35]. These wave functions, for molecules of the form XH_n, consist on molecular orbitals expressed in terms of slater type functions centered on a common origin which is the atom X, each of them being labelled i (varying from 1 to N).

The molecular orbitals are written as:

$$\varphi_i(\vec{r}) = \sum_{k=1}^{N_i} a_{ik}\Phi^{\xi_{ik}}_{n_{ik}l_{ik}m_{ik}}(\vec{r}) \tag{9}$$

where N_i is the number of Slater functions used in the development of the i^th molecular orbital and a_{ik} the weight of each real atomic component

In Eq. (9), $\phi^{\xi_{ik}}_{n_{ik}l_{ik}m_{ik}}(\vec{r})$ is written as

$$\Phi^{\xi_{ik}}_{n_{ik}l_{ik}m_{ik}}(\vec{r}) = R^{\xi_{ik}}_{n_{ik}}(r)S_{l_{ik}m_{ik}}(\hat{r}) \tag{10}$$

where the radial part $R^{\xi_{ik}}_{n_{ik}}(r)$ is given by

$$R^{\xi_{ik}}_{n_{ik}}(r)=\frac{(2\xi_{ik})^{n_{ik}+1/2}}{\sqrt{(2n_{ik})!}}\,r^{n_{ik}-1}e^{-\xi_{ik}\gamma} \tag{11}$$

and where $S_{l_{ik}m_{ik}}(\hat{r})$ is the so-called real solid harmonic [35] expressed by

$$\begin{cases} if\ \ m_{ik}\neq 0: & S_{l_{ik}m_{ik}}(\hat{r})=\left(\dfrac{m_{ik}}{2|m_{ik}|}\right)^{-1/2}\left\{Y_{l_{ik}-|m_{ik}|}(\hat{r})+(-1)^{m_{ik}}\left(\dfrac{m_{ik}}{|m_{ik}|}\right)Y_{l_{ik}|m_{ik}|}(\hat{r})\right\} \\ if\ \ m_{ik}=0: & S_{l_{ik}0}(\hat{r})=Y_{l_{ik}0}(\hat{r}) \end{cases} \tag{12}$$

And at last we note that $\psi_i(\vec{r}_1,\vec{r}_2)$ must be an antisymetrized state.

Moreover, it is important to note that the wave functions given by Moccia refer, for a particular molecular orientation given by the Euler angles (α,β,γ), to take in account all orientations of the molecule we must integrate over the Euler angles.

III - RESULTS AND DISCUSSION

There are no results up today for (e,3e), (e,3-1e) H_2O reaction both in theoretical calculations or in experiments. We study the process under the experimental conditions of Lahmam-Bennani et al [40] for the (e,3-1e) H_2 and just compare the behaviour of the (Fourth DCS) in H_2 and H_2O.

We also study the (FDCS) profile, under the conditions of Takahashi et al [ ] realized for the (e,3e) H_2, and compare the behaviour of cross sections for the (e,3e) for the two systems (H_2 and H_2O).

For the first one, we consider the case of (e,3-1e) experiment conditions on H_2: electron energies are 612, 500, and 51 eV respectively for the incident, scattered and ejected electrons while the unobserved electron is left with 10 eV. The scattering angle is $\theta_S = 1.5^0$. The first ejected electron (51 eV) is detected at a variable angle. The incident and scattered electrons are described by plane waves, the ejected electrons are described by coulomb waves.

In figure(1) we reproduce our results for the (e,3-1e) H_2 [37], the four-fold cross section has been calculated in the first and the second Born approximations and compared to experimental data of Lahmam-Bennani et al [40].

For this calculation, our model (with the second Born approximation) is able to produce part of the shift of the binary peak in the right direction and also yields a recoil peak closer to the experimental one than the first Born results. The main remaining discrepancy concerns the magnitude of the shift of the binary peak.

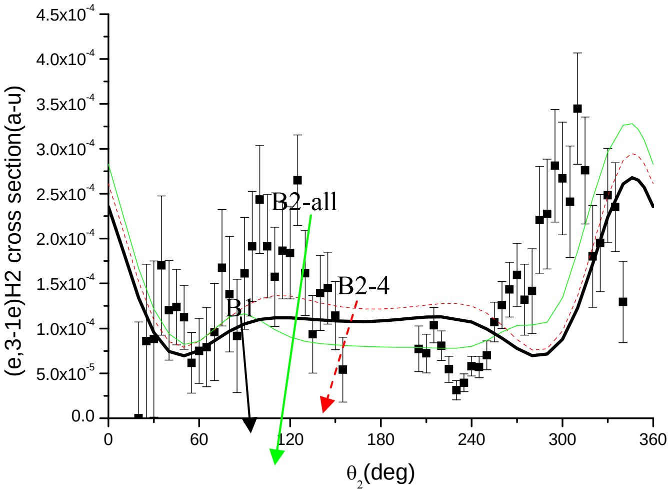


Fig. 1 The four-fold differential cross section in atomic units for the (e,3-1e) double ionisation of H_2.

In the figure, electron energies are 612, 500, and 51 eV respectively for the incident, scattered and ejected electrons while the unobserved electron is left with 10 eV. The scattering angle is $\theta_S = 1.5^0$. The first ejected electron (51 eV) is detected at a variable angle. The results of the first Born treatment including the wave function of Hagstrom and Shull (1959) with 44 terms are represented by a solid (thick) line (B1) and those of the second Born approximation including also the same wave function of Hagstrom and Shull (1959) by a dashed line (only the contribution of the four intermediate states, (B2-4)) and by a solid (thin) line (all contributions, (B2-all), see equation (12)). The experimental data (full squares with error bars, Lahmam-Bennani et al 2002) have been scaled to the theory for the best visual fit at the binary lobe (around 310 deg.).

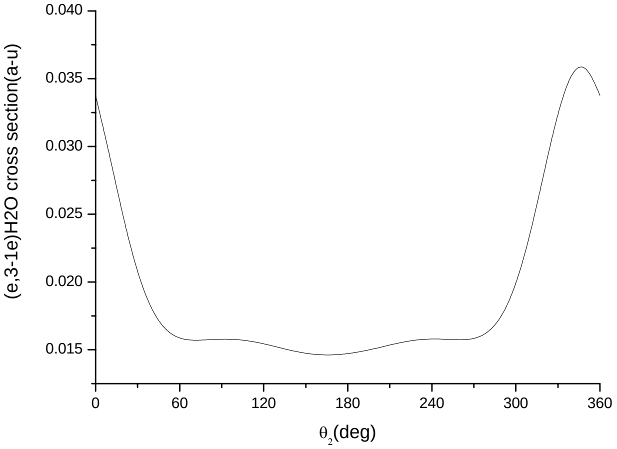


Fig. 2 The four-fold differential cross section in atomic units for the (e,3-1e) double ionisation of H_2O. Electron energies are 612, 500, and 51 eV, respectively for the incident, scattered and ejected electrons while the unobserved electron is left with 10 eV. The scattering angle is $\theta_S = 1.5^0$. The first ejected electron (51 eV) is detected at a variable angle.

In spite of some differences, we notice that the behavior of the two curves is the same.
Our main remark is that the four-fold cross section is bigger in magnitude for the case of H_2O, and then we think that the experiment will be easier to perform than (e,3-1e) H_2.
There are no (e,3e) experiments on H_2 also up to now. Our aim is to use our calculations as a predictive tool to find out and pin point favourable situations for future experiments.
The first Born (e,3e) results obtained for all the situations of the double ionization, as an example we report here calculation done for the 1b1 shell (the two electrons are ejected from the 1b1 shell) for the kinematical conditions: $E_i = 1000$ eV, $E_s = 938.7$ eV, $E_1 = 10$ eV , $E_2 = 10$ eV and a scattering angle ($\theta_S = 1.5$ deg), which corresponds to a medium-small momentum transfer K= 0.3 au in the direction $\theta_k = 330$ degrees in Figure 3 in the form of a 3-D diagram, which allows to easily pin point the most favorable situations for future (e,3e) experiments. This 3-D diagram is dominated by two large structures: (i) the maximum of the cross section occurs at (θ_1 , θ_2) = (279.5°, 40.3°) and at (θ_1 , θ_2) = (220.3°, 79.2°). On the other hand, we also make three observations from the 3D diagram of Figure 3: first, the diagonal line marked $\theta_1 = \theta_2 \pm 50°$corresponds to almost zero intensity, due to the Coulomb repulsion which forbids the two electrons to escape together in the same direction. This is a strict zero because of equal energies E_1 and E_2. Second, the diagonal line marked $\theta_1 = - \theta_2$ corresponds to a small though not vanishing intensity, meaning that the emission of both electrons at equal but opposite angles with respect to the incident beam (so-called symmetric geometry in (e,2e) case) is not probable Third, the back-to-back emission of the ejected electrons, i.e. with a mutual angle $\theta_{12} = 180°$, is not forbidden as it is strictly the case in photo-double ionization (PDI) for H_2 [38]. This analysis can be done for all the situations, when ejected electrons are ejected from different shells

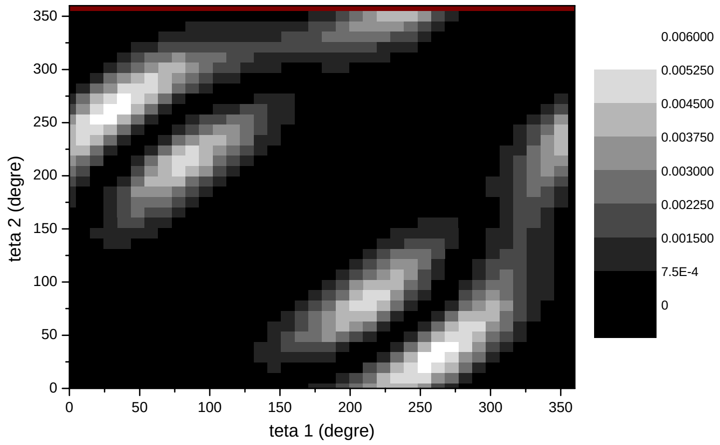


Fig. 3 The variation of the FDCS of the (e,3e) double ionisation of H_2O ionised from the 1b1 shell as a function of the ejection angles θ_1 and θ_2 , in a coplanar arrangement. Incident and scattered electron energies are 1000, and 938.7 eV, respectively, while the ejected electrons energies are $E_1 = 10$ and $E_2 = 10$ eV. The scattering angle is $\theta_S = 1.5^0$.

The next step of our work is to perform another test under other conditions of experiment. We chose for that the conditions of Watanabe et al [39]. We have to use our model for calculate the FourDCS for the (e,3-1e) helium and compared our calculations with the experiment of Watanabe et al [39]. Our results, multiplied by 2, are in good agreement with the experiment. The difference in magnitude is due to the Gamow factor, introduced to describe the repulsion between the ejected electrons in the exit channel. We applied thereafter the model to calculate the FDCS for H_2O under the same conditions of the experiment cited. We notice that the behavior of the two curves is the same, but we have no other results (from experiments or from theories) to confirm the amplitude and the position of the maximum.

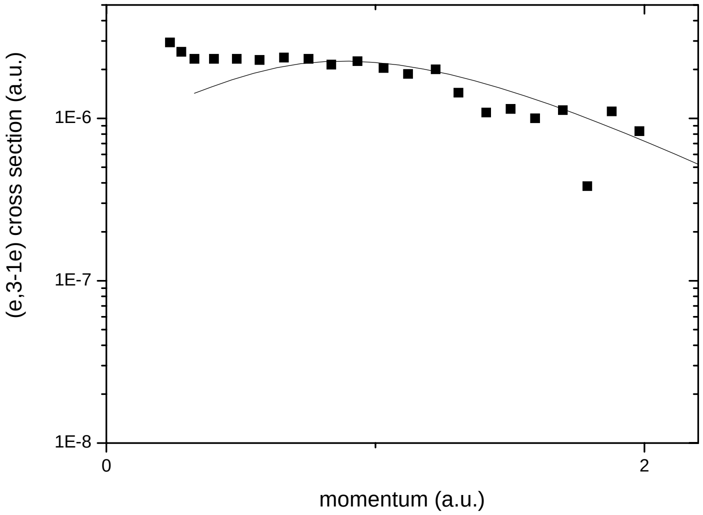


Fig. 4 Comparison of experimental (*e*,3−1*e*) momentum profiles of He for the doubly ionized He2+ with *E*= 10 eV for the non detected electron. The experimental data (full squares) - from Watanabe et al [39].

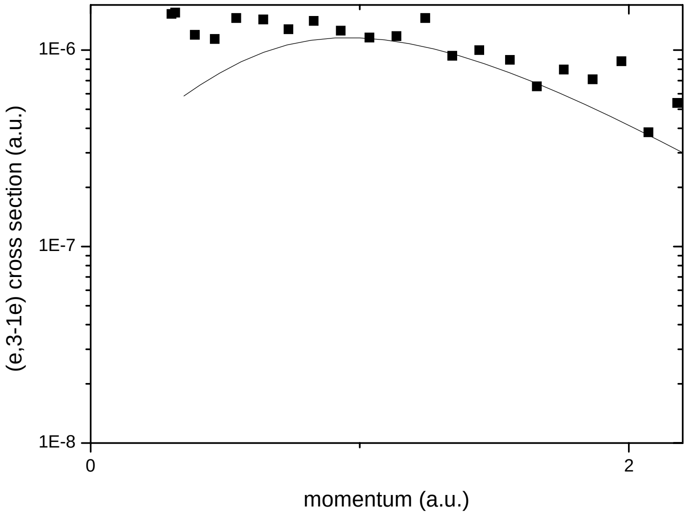


Fig. 5 Comparison of experimental (*e*,3−1*e*) momentum profiles of He for the doubly ionized He2+ with *E*= 20 eV for the non detected electron. The experimental data (full squares) - from Watanabe et al [39].

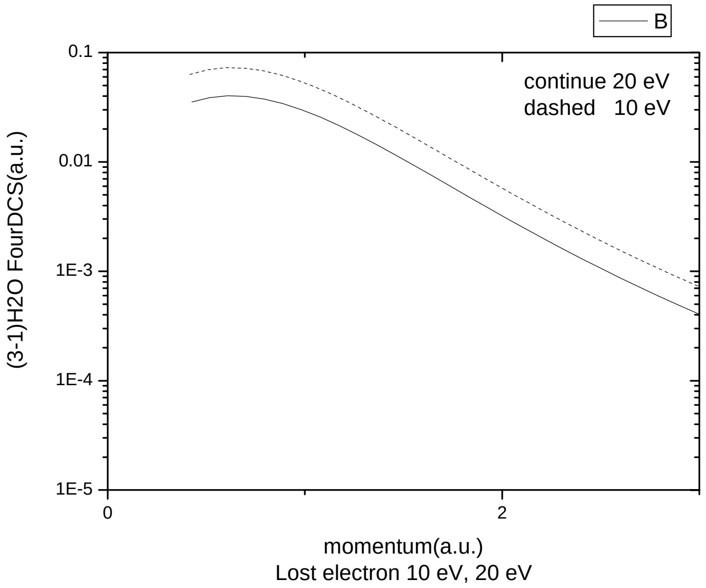
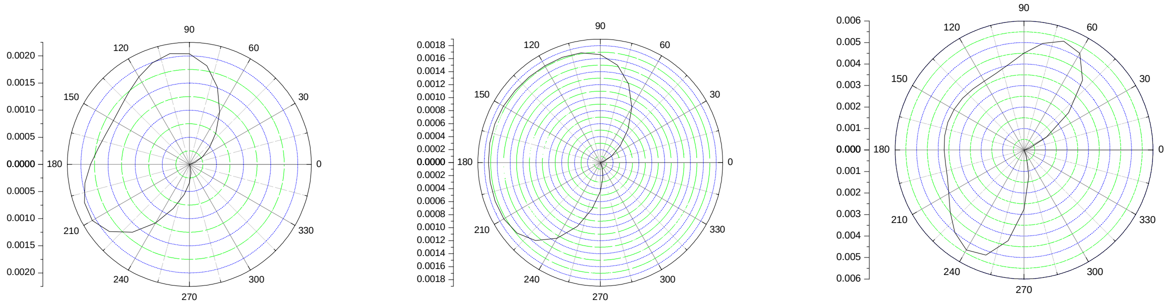


Fig. 6 (e,3−1e) momentum profiles of H_2O for the doubly ionized with *E*= 10,20 eV for the undetected electron. Experiment conditions from Watanabe et al [39].

At last we give in figure (7) the FDCS (e,3e) H_2O for some possibilities of the double ionisation and choose the polar representation for more clearness.



1b1 1b2 3a1-1b2

Fig. 7 Double ionization (e,3e) from different shells of the H_2O molecule. Ionization conditions :
Ei = 1000 eV , E1 =E2 = 10 eV and teta(s)=1° . e1 is ejected with transfer momentum direction.

IV – CONCLUSION

A treatment based on the two coulomb waves Born approximation with the use of highly correlated single-centre wave-functions has been developed to study the (e,3e) and (e,3-1e) double ionisation of H_2O by electron impact. First the model was tested under two experiment conditions for H_2 molecule and atomic Helium. The calculated differential cross sections are compared to the only published (e,3-1e) experiment for the two systems. In the second way we applied the model to calculate the (e,3-1e) and (e,3e) cross sections for H_2O,

As a first conclusion, we note that the (e,3-1e) and (e,3e) experiments might be able to reveal if the first Born treatment is sufficient to describe the process.

We are looking for experimental results and other theoretical calculations to compare our model.

The next step would be to include more accurate intermediate states, or to directly apply a model where the scattered electron is described by a Coulomb wave which in fact includes the interaction between this electron and the target, and describe better the ejected electron in the field of the two-center Coulomb potential.

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