Low energy electron and positron impact differential cross sections for the ionization of water molecules in the coplanar and perpendicular kinematics

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ABSTRACT

We report here triply differential cross sections (TDCSs) for 81 eV electron and positron-impact ionization of the combined ($1b_1$ + $3a_1$) orbitals of the water molecule by using the second-order distorted wave Born approximation (DWBA2) for ejection electron and positron energies of 5 eV and 10 eV and different momentum transfer conditions. The electron-impact TDCS will be compared with the experimental data measured by Ren *et al.* [Phys. Rev. A **95**, 022701 (2017)] and with the molecular 3-body distorted wave (M3DW) approximation results in the scattering plane as well as the perpendicular plane. The DWBA2 results are in better agreement with the experiment than the M3DW results for the scattering plane, and the M3DW results are somewhat better for the perpendicular plane. This observation is explained in terms of collision interactions. The electron and positron TDCSs are indistinguishable in the scattering plane. In the perpendicular plane, the positron results are similar in shape, but smaller in magnitude. However, the difference reduces with increasing projectile scattering angle and increasing ejected electron energy.

I. INTRODUCTION

Charged particle interaction with matter is of interest in many research areas such as astrophysics, atmospheric modeling, plasma physics, discharge physics, medical physics, and radiobiology. In this context, triply differential cross sections (TDCSs) for electron impact single ionization have become a powerful tool for investigating the complete dynamics of the (*e*,2*e*) collisional process. Indeed, the TDCSs provide the most detailed set of information about the ionization process since the full details of the collisions are determined.

In recent years, there has been tremendous progress in describing the electron-impact ionization dynamics of simple atoms and molecules.[1–8] Nowadays, a lot of experimental data are available for electron impact single ionization of simple and complex atomic and molecular targets.[9–11] However, many-body problems still remain unsolved. In this context, several theoretical models have been developed in last decades to describe the ionization processes at different projectile energies and various geometries.[12–16] Various theoretical models and approximations have been suggested, and experiments play a key role for determining the accuracy of the theoretical approximations.

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The problem of single ionization of molecular targets is complicated by the multicenter nature of the target. In principle, the multicenter nature of the target needs to be treated in both the initial and final channels. The standard approach for reducing the many body problem to a manageable 3-body problem is to treat the target as having one active electron with the remaining electrons being passive. Consequently, the multicenter aspects of the collision need to be taken into account in the calculation of the active electron wave function in both the initial and final channels. In the incident channel, one must take the multicenter effects into account in the calculation of the bound state wave function for the active electron. The easiest approach consists in approximating the bound state wave function for the active electron by a single center expansion. There are powerful computer codes available which can provide an accurate description of the molecular ground state in terms of a linear combination of atomic orbitals (LCAO).[17] This method is relatively easy to implement and has been shown to yield fairly accurate results. A more accurate numerical method is the density functional theory (DFT) approach.[18,19] However, from a practical point of view, these wave functions are more computationally intensive to use.

In the final channel, the multicenter nature of the problem is typically approximated as an effective charge or a screened effective charge located at the center of mass. In the Distorted-Wave-Born Approximation (DWBA), the continuum electron moves in an effective field produced by the residual ionic core, screened by the other passive electrons of the target. The molecular 3-body distorted wave (M3DW) approach[20,21] takes the multicenter effect into account by using a spherically symmetric effective charge for the electrons plus a nuclear potential which depends on the location of the nucleus relative to the center-of-mass. The nuclear contribution for one of the nuclei is determined by placing the nuclear charge on a thin shell whose radius is the distance of the nucleus from the center-of-mass and the total nuclear potential is the sum of these potentials summed over all nuclei in the molecule. The multi-center distorted wave approach (MCDW) uses a more sophisticated model in which the location of the nuclei is taken into account in the solution of the Schrödinger for the ejected electron.[22]

The MCDW results show good agreement with the experiment in full three-dimensional kinematics concerning both the angular dependence and the relative magnitude of the cross sections over a large range of analyzed angle and energy conditions for electron impact ionization of water.[23] Whereas the present paper deals with single ionization created by light projectiles, there is also a long history of single ionization created by heavy particle impact. One of the most successful methods for heavy particles is the continuum distorted wave-Eikonal initial state approach state (CDW-EIS) approach of Crothers and McCann.[24] The CDW-EIS has been extended to also include a distorted wave treatment of the ejected electron by Foster *et al.*[25] The CDW-EIS description has also been recently applied to electron-impact ionization of H_2O at low impact energies, and the results are in very good agreement with the experimental data for coplanar geometries.[26]

Studying the interaction between charged particles and the water molecule is of prime importance due to its practical applications in medicine, in radiobiology, and in medical imaging (in particular, for the positron emission tomography, PET).[27] Low-energy electrons are abundantly produced both by X-ray absorption and during radio-therapeutical treatments. Since water represents about 80% of the mass of the human body, the present charged particle track structure codes for modeling the radio-induced damages in biological samples use water to model human tissue.[28,29] In addition to water, complete kinematics studies for ionization of other molecules of biological interest are of importance for future more advanced particle track structure codes. For more details, we refer the reader to our previous studies, namely, Refs. 30 and 31 and references therein for electrons in water vapor and Ref. 32 for electrons in liquid water, as well as Ref. 33 and references therein for positrons in water.

In this context, we have previously performed TDCS calculations for electron and positron collisions in water for symmetric kinematics.[34] The results were in reasonably good agreement with the experimental data, especially for low-electron ejection energies.

In this study, we examine the influence of the projectile charge on the triple differential cross sections for electron- *vs* positron-induced ionization of the sum of $(1b_1 + 3a_1)$ molecular orbitals of the H_2O molecule in coplanar asymmetric and perpendicular plane kinematics within the second-order distorted wave Born approximation (DWBA2) formalism for a relatively low incident energy of 81 eV. The DWBA2 represents an improved version of the distorted wave Born approximation (DWBA) by including the second order Born approximation term. We have also taken into account the post-collisional interaction (PCI), the correlation-polarization effect, and the electron exchange phenomenon. The calculations will be compared with the experimental data of Ref. 35 as well as the theoretical predictions of the molecular 3-body distorted wave approximation (M3DW).[20,21]

We briefly outline the theoretical model in Sec. II and discuss the obtained results in Sec. II. Atomic units ($\hbar = e = m_e = 1$) have been used.

II. THEORY

The electron- and positron-impact single ionization process of water molecules (H_2O) is defined as

$$e^-/e^+ + H_2O \rightarrow H_2O^+ + e^- + e^-/e^+. \quad (1)$$

A. The water molecular wave functions

The target (H_2O) molecular orbitals are here expressed in terms of Slater-like functions all centered at a common origin, i.e., the heaviest atom,[36] namely,

$$\Psi_i(\mathbf{r}) = \sum_{j=1}^{N} a_{ij} \varphi_{n_{ij} l_{ij} m_{ij}}^{\xi_{ij}}(\mathbf{r}), \quad (2)$$

where N_i refers to the number of Slater orbitals $\varphi^{\xi_{ij}}_{n_{ij}l_{ij}m_{ij}}(\mathbf{r})$ and a_{ij} refers to the weight of each atomic component.

The atomic orbitals are expressed as

$$\varphi^{\xi_{ij}}_{n_{ij}l_{ij}m_{ij}}(\mathbf{r}) = R^{\xi_{ij}}_{n_{ij}l_{ij}}(r) S_{l_{ij}m_{ij}}(\hat{r}), \tag{3}$$

where $R^{\xi_{ij}}_{n_{ij}l_{ij}}(r)$ refers to the radial part given by

$$R^{\xi_{ij}}_{n_{ij}l_{ij}}(r) = \frac{(2\xi_{ij})^{2n_{ij}+1/2}}{\sqrt{2n_{ij}!}}\, r^{n_{ij}-1} e^{-\xi_{ij} r}, \tag{4}$$

while the angular part $S_{l_{ij}m_{ij}}(\hat{r})$ denotes the so-called real solid harmonics[37] that may be linked to the complex harmonics via the following expression:

$$\begin{cases} \text{if } m_{ij} \neq 0 \Rightarrow S_{l_{ij}m_{ij}}(\hat{r}) = \left(\dfrac{m_{ij}}{2|m_{ij}|}\right)^{1/2} \left\{ Y_{l_{ij}-|m_{ij}|}(\hat{r}) + (-1)^{m_{ij}} \left(\dfrac{m_{ij}}{|m_{ij}|}\right) Y_{l_{ij}|m_{ij}|}(\hat{r}) \right\}, \\ \text{if } m_{ij} = 0 \Rightarrow S_{l_{ij}m_{ij}}(\hat{r}) = Y_{l_{ij}m_{ij}}(\hat{r}), \end{cases} \tag{5}$$

where $\hat{r}$ designates the solid angle direction.

All the needed parameters and quantum numbers are taken from Ref. 36, and for more details, we refer the reader to Refs. 38–40.

The accuracy of the current single-center expansion in terms of Slater functions has been checked by comparing with the experimental values for some molecular properties [e.g., the binding length O–H, the equilibrium distance H–H, the molecular angle H–O–H, the electric dipole moment, and the 1st ionization potential (IP) of the molecule, see, for example, Ref. 36] as well as the electronic distributions of the four outermost sub-shells of the molecule. Additionally, we used the present wave functions to calculate TDCS to compare with the experimental electron momentum spectroscopy (EMS) measurements (see Ref. 30). These experiments are generally performed for energies in the (1–2 keV) range in a noncoplanar geometry with two outgoing electrons having the same energy and detected at equal polar angles with respect to the incident electron. Under these conditions, the measured TDCSs are directly proportional to the square of the spherically averaged electron momentum distribution which can be obtained from the Fourier transform of the coordinate space wave function. The obtained TDCSs for ionization of the $1b_1$, $3a_1$, $1b_2$, and $2a_1$ orbitals were in very good agreement with the experiment. This clearly indicates that the present bound state wave function for the target is of good quality and constitutes an accurate description of the target structure (see Ref. 30).

B. The electron impact ionization cross section model

The triple differential cross section (TDCS) for the ionization of a molecular target H_2O in the framework of the second order distorted wave Born approximation DWBA2 method is given as

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_2} = (2\pi)^4 \frac{k_1 k_2}{k_0} \sum_{av} |f_{B1} + f_{B2}|^2, \tag{6}$$

where $d\Omega_1 = \sin\theta_1 d\theta_1 d\varphi_1$ and $d\Omega_2 = \sin\theta_2 d\theta_2 d\varphi_2$ denote the solid angle for the scattered and the ejected electron, respec-tively, whereas the energy interval of the ejected electron is represented by dE_2. The momentum of the incident, scattered, and ejected electrons are denoted by $\boldsymbol{k}_0$, $\boldsymbol{k}_1$, and $\boldsymbol{k}_2$, respectively. They correspond to energies E_0, E_1, and E_2 with $E_0 = E_1 + E_2 + IP$, where IP denotes the ionization potential of the water molecule orbital under consideration. The first-order term f_{B1} and second order term f_{B2} in DWBA are given by

$$f_{B1} = \left\langle \chi_1^{(-)}(\mathbf{k}_1, \mathbf{r}_1) \chi_2^{(-)}(\mathbf{k}_2, \mathbf{r}_0) \left| \left(\frac{Z}{r_1} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_0|} \right) \right| \Psi_i(\mathbf{r}_0) \chi_0^{(+)}(\mathbf{k}_0, \mathbf{r}_1) \right\rangle, \tag{7}$$

$$f_{B2} = \left\langle \chi^{(-)}(\mathbf{k}_1, \mathbf{r}_1) \chi^{(-)}(\mathbf{k}_2, \mathbf{r}_0) \left| V G^+_0 V \right| \Psi_i(\mathbf{r}_0) \chi_0^{(+)}(\mathbf{k}_0, \mathbf{r}_1) \right\rangle, \tag{8}$$

where Z refers to the charge of the ionized target (here $Z = 1$) and G^+_0 is the Green's function defined by

$$G^+_0 = \frac{1}{E_0 - H + i\varepsilon}, \tag{9}$$

where H is the Hamiltonian of the target defined by the relation $H = -\frac{\nabla^2}{2} \pm \left(\frac{Z}{r_1} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_0|} \right)$, and $\varepsilon \to 0^+$.

$\chi_0^{(+)}(\mathbf{k}_0, \mathbf{r}_1)$ is the distorted wave function used for describing the incident particle, while $\chi_1^{(-)}(\mathbf{k}_1, \mathbf{r}_1)$ and $\chi_2^{(-)}(\mathbf{k}_2, \mathbf{r}_0)$ refer to the distorted wave functions used for the two outgoing particles. In the DWBA2 calculation, the initial-state distorted waves are generated using the initial-state distorting potential V constituted from a combination of the nuclear contribution plus a spherically symmetric approxi-mation for the interaction between the incident particle and the target electrons, while the final-state distorted waves are obtained in the final-state distorting potential includ-ing the nuclear contribution plus a spherically symmetric

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approximation for the interaction between the continuum electron and the electrons in the ion.

We have made a careful check to ensure that the cross sections are satisfactorily converged in terms of the partial wave sums. Finally, let us note that the spin-averaged static-exchange potential of Furness and McCarthy[41] as modified by Riley and Truhlar[42] has been used for the case of electron-induced ionization.

C. The positron impact ionization cross section model

For positron impact ionization, the first-order term f_{B1} and the second order term f_{B2} change with the "+" sign for the interaction term in amplitude formulas, namely,

$$f_{B1} = \left\langle \chi_1^{(-)}(\mathbf{k}_1, \mathbf{r}_1)\chi_2^{(-)}(\mathbf{k}_2, \mathbf{r}_0) \left| \left(\frac{Z}{r_1} - \frac{1}{|\mathbf{r}_1 - \mathbf{r}_0|} \right) \right| \Psi_i(\mathbf{r}_0)\chi_0^{(+)}(\mathbf{k}_0, \mathbf{r}_1) \right\rangle, \quad (10)$$

$$f_{B2} = \left\langle \chi^{(-)}(\mathbf{k}_1, \mathbf{r}_1)\chi^{(-)}(\mathbf{k}_2, \mathbf{r}_0) \left| V_0 G_0^+ V \right| \Psi_i(\mathbf{r}_0)\chi_0^{(+)}(\mathbf{k}_0, \mathbf{r}_1) \right\rangle. \quad (11)$$

The distorted wave for the incident positron is calculated using the neutral distorting potential, and the distorted wave for the scattered positron is calculated using the ion potential. On the other hand, the distorted wave for the ejected electron is generated in the static exchange potential of molecular ions.

D. Inclusion of the post-collision interaction (PCI)

We have included PCI in our DWBA calculations using the Ward-Macek factor.[43] In the Ward and Macek approximation, the interaction between the ejected electron and the scattered projectile is approximated by

$$|C_{\text{proj-eject}}|^2 = G|_1F_1(i\gamma, 1, -2ik_{ab}r_{ab}^{\text{ave}})|^2, \quad (12)$$

where G is defined as

$$G = |e^{-\pi\gamma/2}\Gamma(1 - i\gamma)|^2 = \frac{\pi/k_{ab}}{(e^{\pi/k_{ab}} - 1)}. \quad (13)$$

Here Γ is the gamma function, k_{ab} is the relative electron-electron wave number, which depends on the relative velocity v_{ab}, and γ is the Sommerfeld parameter $\gamma = (z_p z_e / v_{ab})$, where z_e and z_p are the charges of the ejected electron and projectile, respectively. The parameter r_{ab}^{ave} (the average separation) is given by $r_{ab}^{\text{ave}} = \frac{\pi^2}{16\varepsilon}(1 + \frac{0.627}{\pi}\sqrt{\ln \varepsilon})^2$, with ϵ being the total energy of the two emerging electrons. Finally, the TDCS including PCI in the Ward-Macek approximation is given by

$$\frac{d^3\sigma}{d\Omega_1 d\Omega_2 dE_2} = |C_{\text{proj-eject}}|^2 (2\pi)^4 \frac{k_1 k_2}{k_0} \sum_{av} |f_{B1} + f_{B2}|^2. \quad (14)$$

III. RESULTS AND DISCUSSION

The electron impact and positron impact triply differential cross sections (TDCSs) for ionization of the sum of the $1b_1$

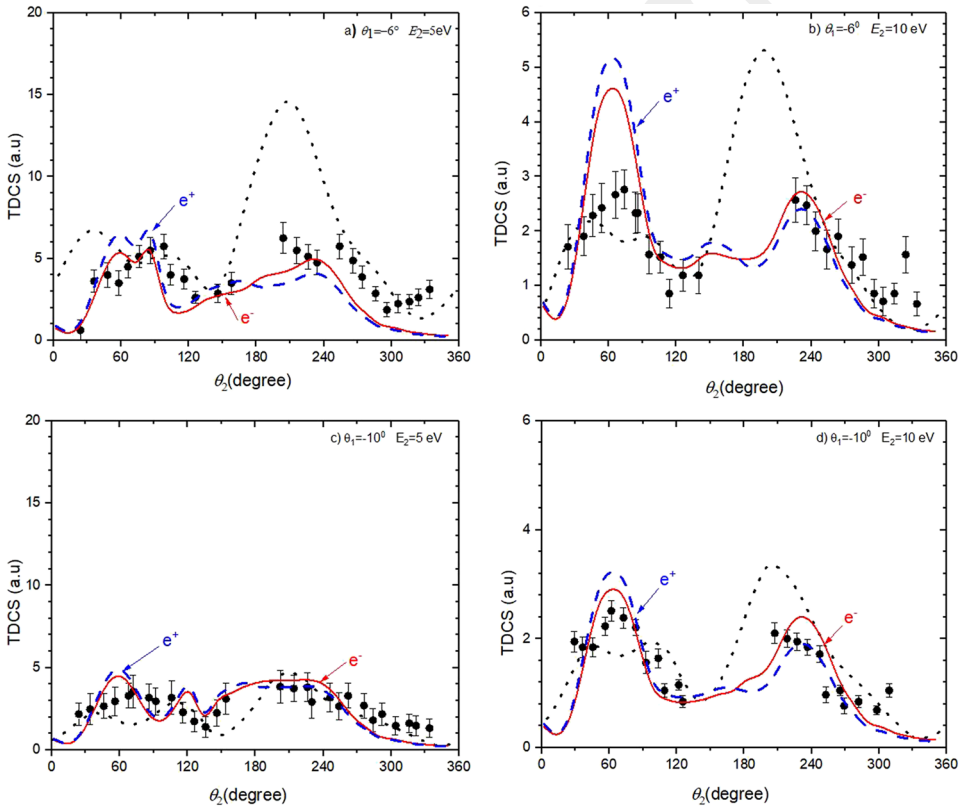


FIG. 1. Triply differential cross sections (TDCSs) for electron and positron impact ionization of the summed ($1b_1$ + $3a_1$) molecular state of the water molecule in a coplanar geometry. The TDCSs are reported as a function of the ejected electron emission angle θ_2 for vari-ous (θ_1, E_2) at a projectile energy E_0 = 81 eV. The TDCSs for the electron impact (red solid line) and positron impact (blue dashed line) have been compared with the existing elec-tron measurements[35] (solid circles) and the molecular 3-body distorted wave (M3DW) using a proper average over all orientations[35] (dotted line). The exper-imental and theoretical data have been both normalized to each other.

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and $3a_1$ orbitals are shown in Fig. 1 for scattering angles –6° and –10° and ejected electron energies of 5 eV and 10 eV. The TDCSs for the electron impact (red solid line) and positron impact (blue dashed line) have been compared with the measurements[35] (solid circles) and the molecular 3-body distorted wave (M3DW) using a proper average (PA) over all orientations[35] (dotted line). All the theoretical results reproduce the two distinct regions experimentally observed in the structure of the TDCS, namely, the binary and recoil regions. Overall, the DWBA2 is in reasonably good agreement with the experiment. The DWBA2 calculations (solid lines) predict nearly the same magnitude for the binary and recoil peaks as is seen in the measurements,[35] except for an ejected elec-tron energy of 10 eV and a scattering angle of –6° [Fig. 1(b)] where the DWBA2 results predict the binary peak to be much larger than the recoil peak. For the smaller scatter-ing angle (6°), the M3DW results predict a larger recoil peak than the binary peak contrary to the experimental measure-ments, while for the larger scattering angle (10°), the binary and recoil peaks are of similar magnitude in better agreement with the experiment. The current DWBA2 calculations as well as the M3DW calculations show a double binary peak struc-ture at an ejected electron energy of 5 eV. The measurements do not show the theoretically predicted double binary peak structure; however, the measurements do exhibit a minimum around an ejected electron angle of 120° that is also repro-duced by both theories. The M3DW also predicts a double binary peak for an ejected electron energy of 10 eV, while both the DWBA2 and experiment exhibit only a single binary peak.

Overall, the DWBA2 results are in better agreement with the experiment that the M3DW for electron-impact ionization in the scattering plane. Both calculations treat the continuum electrons as waves distorted by the Coulomb field of the target. The M3DW is a first order calculation that contains the post collision interaction (PCI) to all orders of perturbation theory. The DWBA2 is a second order calculation that approximates PCI using the Ward-Macek approximation. PCI should be most important when the two ejected electrons have comparable energies. However, for this case, the ejected electron energies are 5 eV and 10 eV, so it is reasonable to assume that PCI might not be a dominant interaction. The other difference is the first order *vs* second order (i.e., the projectile "hits" the target either once or twice). The fact that the DWBA2 results are in better agreement with the experiment indicates that the second order contributions are more important than PCI for these kinematics.

The current positron impact TDCS results (dashed blue line) are very similar to the electron impact TDCS (solid red curve). In fact, the electron and positron results are indistinguishable to within the experimental error. Similar results been observed for the case of atoms.[44,45]

The TDCSs for electron-impact ionization of a water molecule in the perpendicular geometry are shown in Fig. 2.

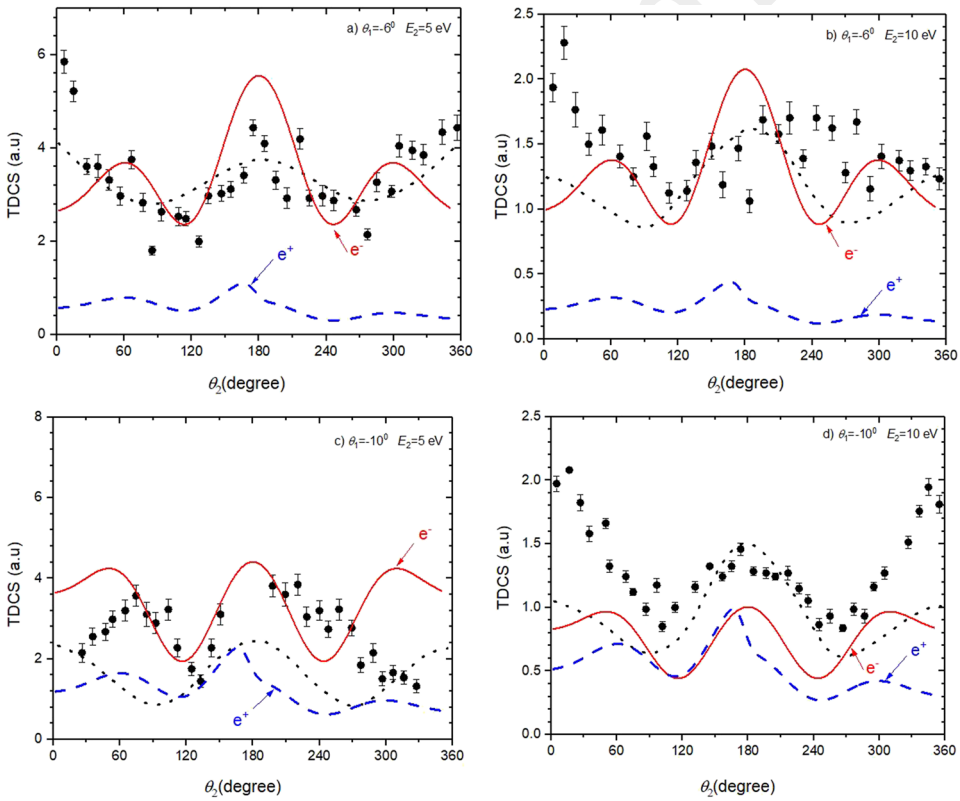


FIG. 2. Same as in Fig. 1 for the perpen-dicular plane geometry.

The current DWBA2 results are compared with the electron measurements taken from Ref. 35 as well as the theoretical M3DW TDCSs. In all cases, both the experiment and the-ory exhibit a peak at 180° and in three of the four mea-sured cases, the experimental data found a significantly larger peak at 0° (360°). The DWBA2 predicts a peak around 60° for all four measured cases and no peak at 0°. For the case of (5 eV, 10°), the experiment also has a peak not at 0°. How-ever, it is located at a larger angle than predicted by the DWBA2. On the other hand, the M3DW predicts 0° peaks in all four cases. However, the peaks are not as large as the experimentally measured ones. Overall, the M3DW results are probably in somewhat better agreement with the experiment due to the prediction of the 0° peaks. For an electron to be ejected into the perpendicular plane logically requires a deeper penetration of the projectile into the target charge density (closer collisions). The fact that the M3DW is in better agreement with the experiment suggests that the final state electron-electron interaction is more important when both electrons are close to the target (and presumably close to each other) and this interaction is then more important than double collisions.

The positron impact TDCSs have also been calculated and compared with the electron impact measurements and theoretical results. For the smaller projectile scattering angle, the positron TDCS is about a factor of 5 smaller than the corresponding electron results. However, the shapes of the two TDCS are very similar. For the larger projectile scattering angle, the difference reduces to a factor of 3 for the 5 eV ejected electrons while the positron results have comparable magnitudes to the electron results for 10 eV ejected electrons. Nevertheless, the shape of the electron and positron results is still very similar.

IV. CONCLUSIONS

We have reported DWBA2 TDCS for electron and positron impact ionization of water molecules. The theoretical results have been compared with the available experimental results for electron-impact ionization as well as the previously published molecular 3-body distorted wave (M3DW) results. The experiment and theory were compared for the ejected electron being detected in both the scattering plane and the perpendicular plane. For the scattering plane, the DWBA2 results were in better agreement with the experiment than the M3DW. The M3DW is a first order theory which includes the post collision interaction (PCI) to all orders of perturbation theory. The DWBA2 is a second order theory which includes PCI approximately. PCI should be most important when both final state electrons have the same speed which is not the case for the present kinematics. Consequently, the scattering plane results indicate that second order (2 hits) are more important than the long-range PCI effects for these kinematics.

On the other hand, the M3DW results were in better agreement with the experiment than the DWBA2 for the perpendicular plane. One would expect that a deeper penetration of the target charge cloud would be required to eject an electron into the perpendicular plane. A deeper penetration would mean closer electron-electron interactions for which PCI would then be important. Consequently, the perpendicular plane results indicate that PCI is more important than double hits if the projectile electron penetrates significantly into the charge cloud. Presumably, for the scattering plane, glancing collisions dominate and two hits become more important than PCI.

There are no experimental TDCS data available for the ionization of water by positron impact. Nevertheless, we have compared our results obtained for this projectile with the electron cross sections. Our results indicate that the shape of the TDCS is very similar for both the electron and positron impact. In the scattering plane, the electron and positron results are identical to within the experimental error. In the perpendicular plane, the shapes were similar, but the positron results were about a factor of 5 smaller than the electron results for the smaller projectile scattering angle. For the larger scattering angle, the difference was smaller and the difference decreased with increasing ejected electron energy.

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