



Electron-Impact Single Ionization of Molecules: Orientation-Resolved Fully Differential Cross Sections [†]

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Abstract

In this work, we study the single ionization of H₂O and C₄H₈O by electron impact. Fully differential cross sections are calculated by means of two distorted wave models which vary in the single-centre approximation applied to the interaction of the continuum electrons with the residual molecular ion. Dependence on the molecular target orientation is analyzed before performing an average procedure to benchmark with experimental data. The present results suggest that structures in non-oriented triple differential cross sections do not directly reflect the patterns inferred from a limited set of particular orientations, demanding an extensive averaging procedure.

Keywords: ionization; electron impact; molecular targets; fully differential cross sections

1. Introduction

Interactions of electrons with water and biomolecules are of special relevance in the context of radiotherapy, since high-energy radiation produces large numbers of low- and intermediate-energy secondary electrons, which are largely responsible for subsequent molecular damage [1]. A complete characterization of electron-impact single ionization processes, known in the literature as (e, 2e), is achieved through the analysis of fully differential cross sections (FDCSs), which depend on all kinematic variables of the collision except for spin, therefore providing the most stringent test for theoretical descriptions. However, while highly accurate nonperturbative approaches have been successfully applied to simple atoms and small molecules [2,3], their extension to polyatomic and multielectron systems is severely limited by the rapid growth in computational complexity. As a consequence, theoretical studies of molecules such as H₂O and larger organic species have predominantly relied on perturbative frameworks. Among these, distorted-wave methods have become the standard tools for analyzing single ionization by electron impact, proving a robust capability to reproduce essential features of measured FDCSs over a broad range of kinematic conditions [4–9].

From an experimental point of view, highly differential cross section measurements have evolved over several decades, progressing from early studies that were limited to relative shapes [10,11] toward modern kinematically complete experiments capable of accessing large regions of phase space [12–16]. Unfortunately, experimentally resolving the molecular orientation at the moment of the collision is still very challenging [17], in contrast to predictions from perturbative models where the FDCS calculation for a



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particular orientation of the molecular target is more straightforward than averaging over all molecular orientations [18].

In this work, we analyze the electron-impact single ionization of H₂O and the deoxyribose sugar molecular analogue C₄H₈O at intermediate-to-low impact energies. FDCSs are calculated by means of two theoretical approximations under the framework of the CDW-EIS model, which has previously shown good overall agreement with experimental data for water targets [7]. Here, we provide a more detailed analysis of these theoretical approaches, already employed in Ref. [18], by analyzing their differences at the continuum electron wave function level and focusing on the molecular orientation dependence of the FDCSs. In addition, we perform an average procedure to benchmark our results with recent experimental data obtained by means of the “Cold Target Recoil Ion Momentum Spectrometer” (COLTRIMS) technique [15,16]. This experimental method allows for the simultaneous detection of the three particles in the final state (two continuum electrons and the recoil ion with total charge +1). In this sense, the experimentalists can isolate single ionization events, with no contribution from multiple ionization.

Section 2 provides a concise overview of the theoretical methods adopted in the present study. The obtained results are presented and discussed in Section 3. Unless explicitly indicated, all quantities are expressed in atomic units throughout this work.

2. Materials and Methods

The (e, 2e) collision process considered in this work is analyzed under the framework of the distorted wave formalism and the one active electron approximation, with its transition amplitude given by

$$T_{fi} = \langle \Psi_f^- | W_f | \Psi_i^+ - \psi_i \rangle + \langle \Psi_f^- | V_i | \psi_i \rangle, \quad (1)$$

which is the following version of the Gellman–Goldberger amplitude. Although the wave functions and perturbation operators in Equation (1) were previously described in detail [18], in what follows we will focus on the main differences between the two theoretical models employed in this work, which differ only in the final state of the collision. It is worth mentioning that for the initial wave function Ψ_i^+ , we consider the Eikonal Initial State (EIS) which retains the long-range Coulomb potential effects, and the post-collisional interaction (PCI) between the continuum particles is fully considered in both models.

The interaction of the continuum electrons with the residual molecular ion is described with distorted waves $\chi^-(\mathbf{k}_i, \mathbf{r}_i)$, eigenvalues of the molecular anisotropic potential, which in this work we approximate by a single-centre potential $V_{1C}(r_i)$ ($i = 1$ for the projectile and $i = 2$ for the secondary electron initially bound to the target). Hence, a partial wave expansion can be applied to these distorted waves which are then separated in a radial and an angular part as follows

$$\chi^-(\mathbf{k}_i, \mathbf{r}_i) = \sum_{l=0}^{\infty} \frac{(2l+1)}{k_i r_i} i^l e^{-i\sigma_l} u_l(k_i, r_i) P_l(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{r}}_i), \quad (2)$$

where $\sigma_l = \sigma_l^{Coul} + \delta_l$, with δ_l being the non-Coulombic phase shift in the radial waves ($\delta_l = 0$ for a pure Coulomb central potential) and $\sigma_l^{Coul} = \arg[\Gamma(l+1+i\alpha_i)]$. $P_l(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{r}}_i)$ are the Legendre polynomials and the radial wave functions $u_l(k_i, r_i)$ satisfy the equation

$$\left[-\frac{1}{2} \frac{d^2}{dr_i^2} + \frac{l(l+1)}{2r_i^2} + V_{1C}(r_i) \right] u_l(k_i, r_i) = \frac{k_i^2}{2} u_l(k_i, r_i). \quad (3)$$

At this point, the single-centre description of the final state of the collision will depend on the choice of $V_{1C}(r_i)$. In this work we perform two different single-centre approximations.

First, we consider the molecular ion as a single-centre of charge $Z_t = +1$, therefore leading to the well known CDW-EIS model, where the radial wave functions are simply solutions to the pure Coulomb potential. A second choice consists of a spherical average (SA) of the anisotropic potential which provides an isotropic description of the molecular ion but retains some information of the spatial charge distribution, an approach which has already been applied in the context of ion collisions with H₂O [19,20]. In what follows we will refer to this model as SADW-EIS. The partial waves $u_l(k_i, r_i)$ are calculated with Salvat's code [21], which permits us to obtain the non-Coulombic phase shifts δ_l as well. These phase shifts become negligible as l increases, and due to the asymptotic limit of these potentials, the radial wave functions converge to the Coulombic ones. In this sense, the infinite partial waves can be accounted for by correcting only a few l -values from the pure Coulomb case.

This strategy considerably reduces the numerical effort of calculating the transition amplitude of Equation (1), which involves a six-dimensional numerical integration. Then, the FDCS for the electron-impact ionization of a molecule and for a particular orientation of the molecular axes defined by the set of Euler angles (α, β, γ) is given by

$$\frac{d^6\sigma}{dE d\Omega_1 d\Omega_2 d\alpha d\beta d\gamma} = N_e (2\pi)^4 \frac{k_1 k_2}{k_0} \left[\frac{1}{4} |T_{fi}^D + T_{fi}^E|^2 + \frac{3}{4} |T_{fi}^D - T_{fi}^E|^2 \right], \quad (4)$$

where N_e represents the number of identical electrons in the molecular orbital to be ionized and T_{fi}^D and T_{fi}^E are the direct and exchange transition amplitudes, with $T_{fi}^E(\mathbf{k}_1, \mathbf{k}_2) = T_{fi}^D(\mathbf{k}_2, \mathbf{k}_1)$. In order to compare our results with experimental data we have to perform an average procedure by integrating over the three Euler angles α , β , and γ to obtain the triple differential cross section (TDCS). We refer the reader to Ref. [18] for more details about the evaluation of this integral.

3. Results and Discussion

In this section we present the calculated FDCS for the electron-impact single ionization of H₂O and C₄H₈O (tetrahydrofuran or THF) by means of the two theoretical methods introduced in the previous sections: the CDW-EIS and the SADW-EIS. We analyze the emission of a 10 eV secondary electron in the final state with an angle θ_2 with respect to the z axis and into the scattering plane xz , defined by the initial and final momenta of the projectile, with a projectile scattering angle of -10° .

3.1. Single Ionization of H₂O

The FDCSs of H₂O are calculated at an impact energy of 65 eV and represent the sum of the emission from the $1b_1$ and $3a_1$ molecular orbitals. Their electronic densities are presented in Figure 1, where it can be seen that they present two well defined lobes, which are characteristic of p -type orbitals.

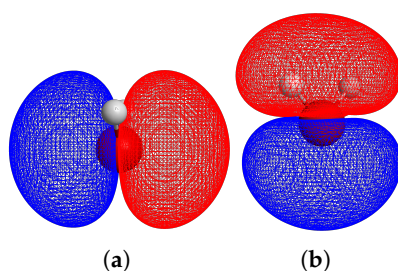


Figure 1. Electronic densities of the (a) $1b_1$ and (b) $3a_1$ molecular orbitals of H₂O.

In Figure 2 we present the partial waves $u_l(k_i, r_i)$, solutions of Equation (3) for the spherical average potential, together with the Coulombic ones corresponding to a centre

of charge $Z_t = 1$, considering an electron emitted from the $1b_1$ molecular orbital with an energy of 10 eV. From these, we observe how the two first partial waves ($l = 0$ and $l = 1$) considerably differ from the case $Z_t = 1$, whereas for $l = 3$, no discrepancies are observed and convergence is achieved. Therefore, it can be seen how the spherical average approximation only modifies the first partial waves of the secondary electron wave function. This is attributed to the centrifugal barrier imposed by the second term in Equation (3) as l increases.

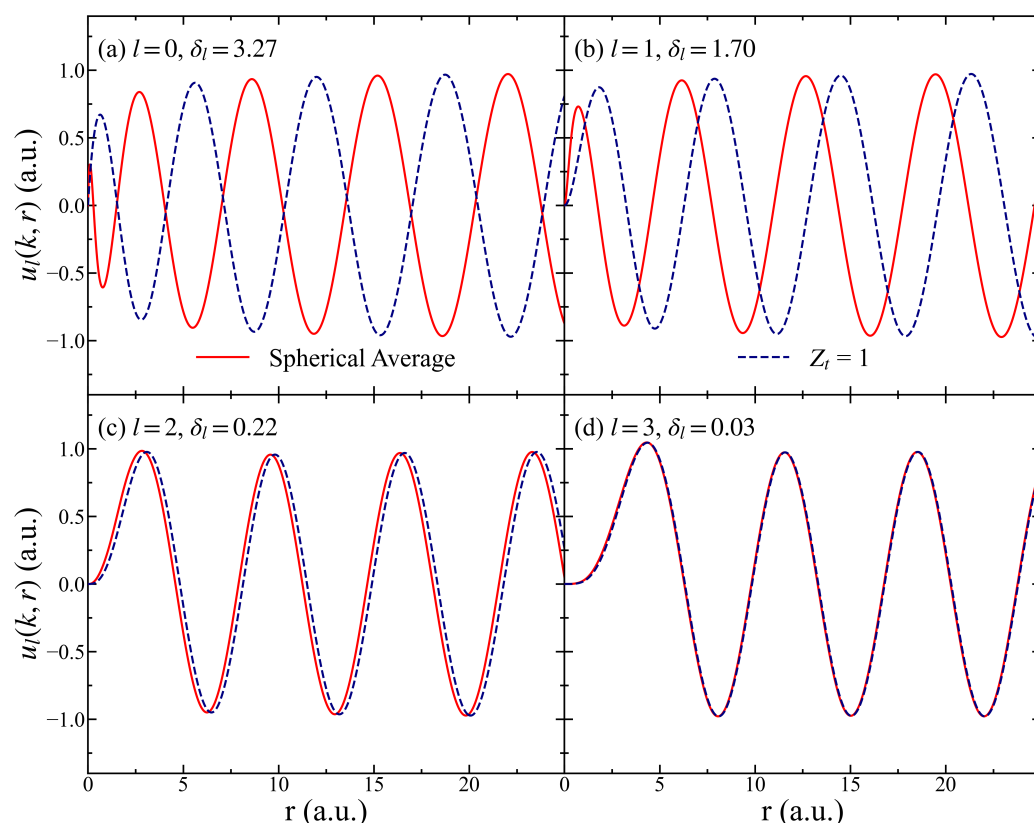


Figure 2. Partial waves, solutions of the spherical average potential (solid line) and the $Z_t = 1$ potential (dashed line) for an electron emitted from the $1b_1$ molecular orbital in the continuum of the H_2O^+ ion, with an energy of 10 eV.

The FDCSs for the single ionization of H_2O are presented in Figure 3 for three different molecular orientations of the target. In the first place, in Figure 3a the orientation is defined by the set of Euler angles $(\alpha, \beta, \gamma) = (0^\circ, 90^\circ, 0^\circ)$. Considering emission into low θ_2 angles, which is known as the binary region, we observe that both models predict a single peak around 60° . Differences between them are observed for emission into large angles, known as the recoil region. There, the CDW-EIS model predicts a broad single peak, whereas the SADW-EIS model presents a shoulder around 180° and a much higher magnitude for the recoil peak. This leads to a higher recoil/binary ratio predicted by the SADW-EIS model, which implies a higher probability that the secondary electron is emitted backwards for this particular orientation.

Another orientation considered in this work is defined by the set of Euler angles $(\alpha, \beta, \gamma) = (0^\circ, 90^\circ, 90^\circ)$ and is exhibited in Figure 3b for the single ionization of H_2O . Here, we observe a two-peak binary structure predicted by both models but with a less deep minimum between the two maxima for the SADW-EIS method. This binary structure is characteristic of ionization of p -type atomic orbitals and tends to show up as momentum transfer increases [22], and, as can be seen in Figure 1, both the $1b_1$ and $3a_1$ molecular orbitals are mostly $2p$ in nature. Therefore it is expected that some orientations present

this binary structure. For the recoil region we observe a high recoil peak predicted by both models around 200° and a much lower one around 300° .

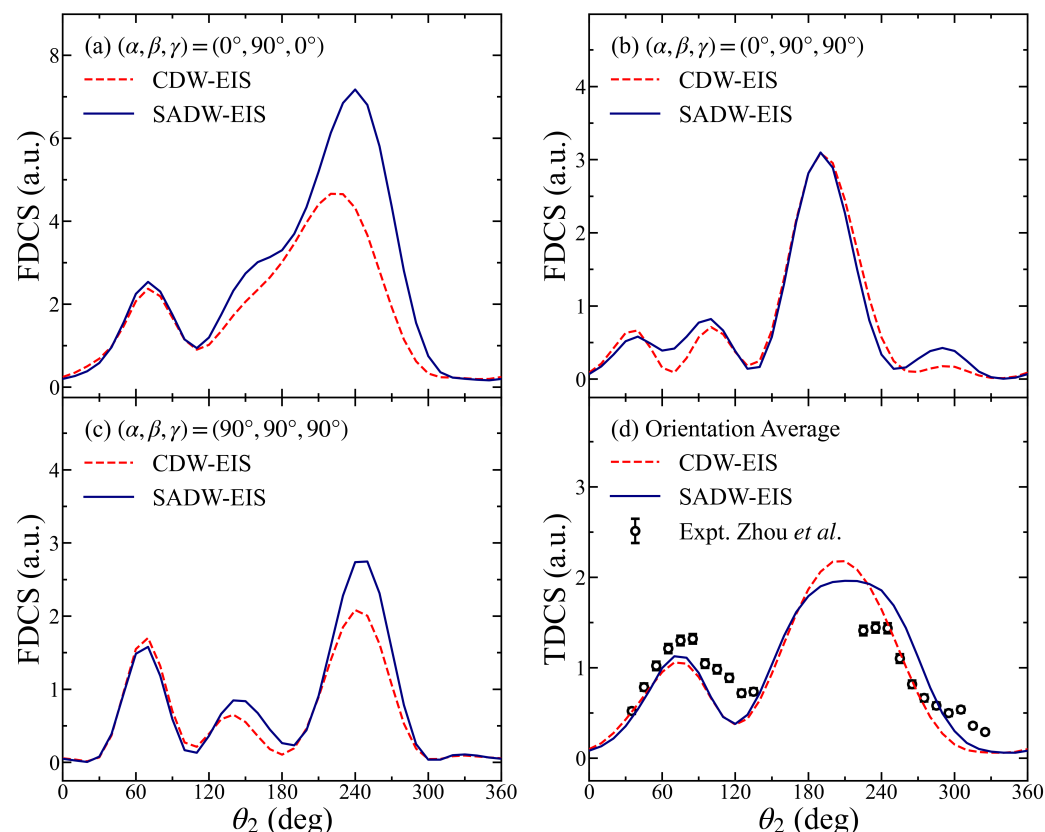


Figure 3. Fully differential cross sections for the single ionization of H_2O by 65 eV electron impact, calculated by means of the SADW-EIS (solid line) and CDW-EIS (dashed line) models, as a function of the emitted electron angle into the scattering plane xz for an electron energy of 10 eV and a projectile scattering angle of -10° and for molecular orientations defined by the set of Euler angles $(\alpha, \beta, \gamma) =$ (a) $(0^\circ, 90^\circ, 0^\circ)$, (b) $(0^\circ, 90^\circ, 90^\circ)$, (c) $(90^\circ, 90^\circ, 90^\circ)$. (d) Triple differential cross sections after averaging over all orientations. Experimental data obtained from Ref. [15].

In Figure 3c the molecular orientation considered is defined by $(\alpha, \beta, \gamma) = (90^\circ, 90^\circ, 90^\circ)$ and again we observe that both models predict very similar structures. Two binary peaks are again predicted but this time with different magnitudes, while we observe a single narrow recoil peak. Once more, the SADW-EIS model predicts a higher magnitude as was seen for the previous orientations.

Finally, in Figure 3d we present the TDCS obtained after analytically averaging over all molecular orientations. We benchmark with recent experimental data reported in Ref. [15], which exhibit well defined binary and recoil structures. The binary region presents a single peak which is well reproduced by both models, suggesting that even though there are particular orientations where two binary peaks are predicted, this structure gets washed out when we average over all molecular orientations, in agreement with the experiment. Regarding the recoil region, we observe that both models slightly overestimate the experimental data with not many differences between them. Interestingly, the recoil magnitude predicted by the SADW-EIS model is lower, in contrast with panels (a), (b) and (c). This indicates that the FDCSs for the particular orientations shown here are not enough to make any conclusions about the orientations' average TDCS. Therefore, in order to make predictions for non-oriented targets it seems to be unavoidable to perform this type of average.

3.2. Single Ionization of C_4H_8O

The FDCSs of THF are calculated at an impact energy of 250 eV and represent emissions from the 9b and 12a' molecular orbitals of the C_2 and C_s conformers, respectively, in a 80%:20% proportion. Their electronic densities are presented in Figure 4, where we observe that they exhibit a lone pair of p -type lobes around the oxygen centre and much more complicated structures around the carbon and hydrogen atoms.

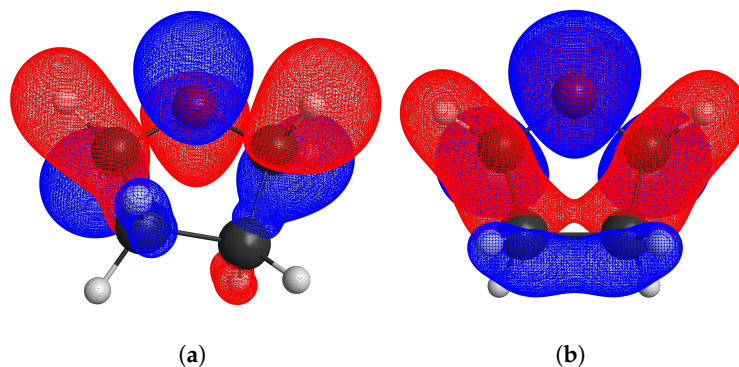


Figure 4. Electronic densities of the (a) C_2 conformation 9b and (b) C_s conformation 12a' molecular orbitals of THF.

In Figure 5 we present the partial waves considering an electron emitted from the 9b molecular orbital of the C_2 conformation with an energy of 10 eV. As for the case of H_2O , the first two partial waves ($l = 0$ and $l = 1$) present great differences between considering a spherical average potential and a single centre of charge $Z_t = 1$. However, convergence as l increases is reached for larger values, in comparison with Figure 2. This can obey the fact that the spherical average potential reaches the asymptotical $Z_t = 1$ charge at higher distances from the molecule due to its larger spatial extension.

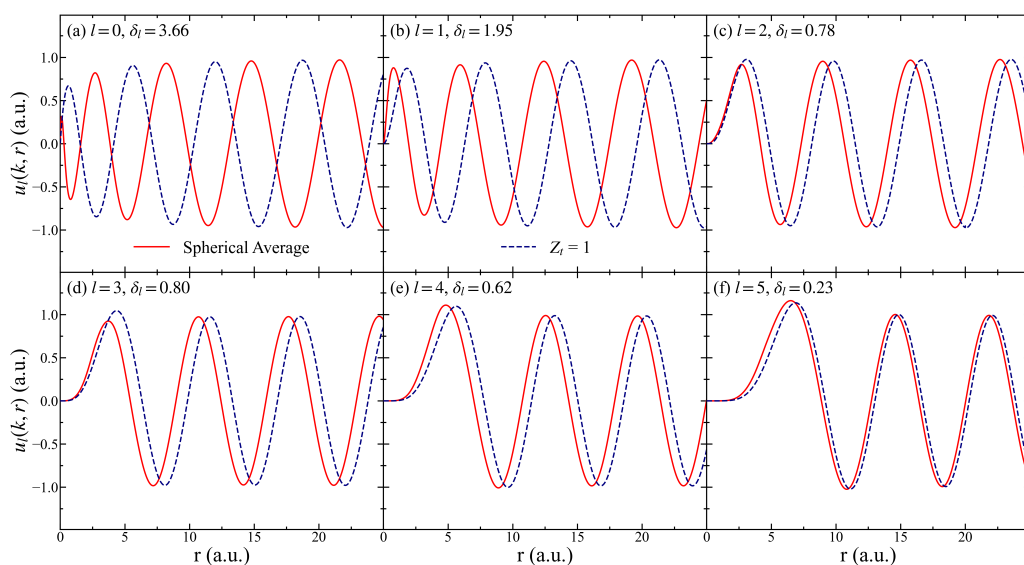


Figure 5. The same as Figure 2 for an electron emitted from the 9b molecular orbital of the C_2 conformation of the THF^+ ion.

The FDCSs for the single ionization of THF are presented in Figure 6 for three different molecular orientations of the target. In panels (a), (b) and (c), the orientations are defined by the same set of Euler angles as in the case of H_2O , but we observe that in this case the structures predicted by the theoretical models are not so well defined. In panel (a) we observe four peaks with minima at values of θ_2 around 90° , 180° and 270° , a structure

that curiously seems to be rather symmetric around 180° . This suggests, for this particular orientation, that binary and recoil emissions have similar probabilities with a higher magnitude predicted by the SADW-EIS model. In contrast, for the orientation shown in panel (b), we observe that this model exhibits a well defined two-peak binary structure with no evidence of recoil emission. For the last orientation considered, in panel (c), we observe a pretty much noisy structure predicted by both models with several peaks along the whole angular range, but with different positions and magnitudes.

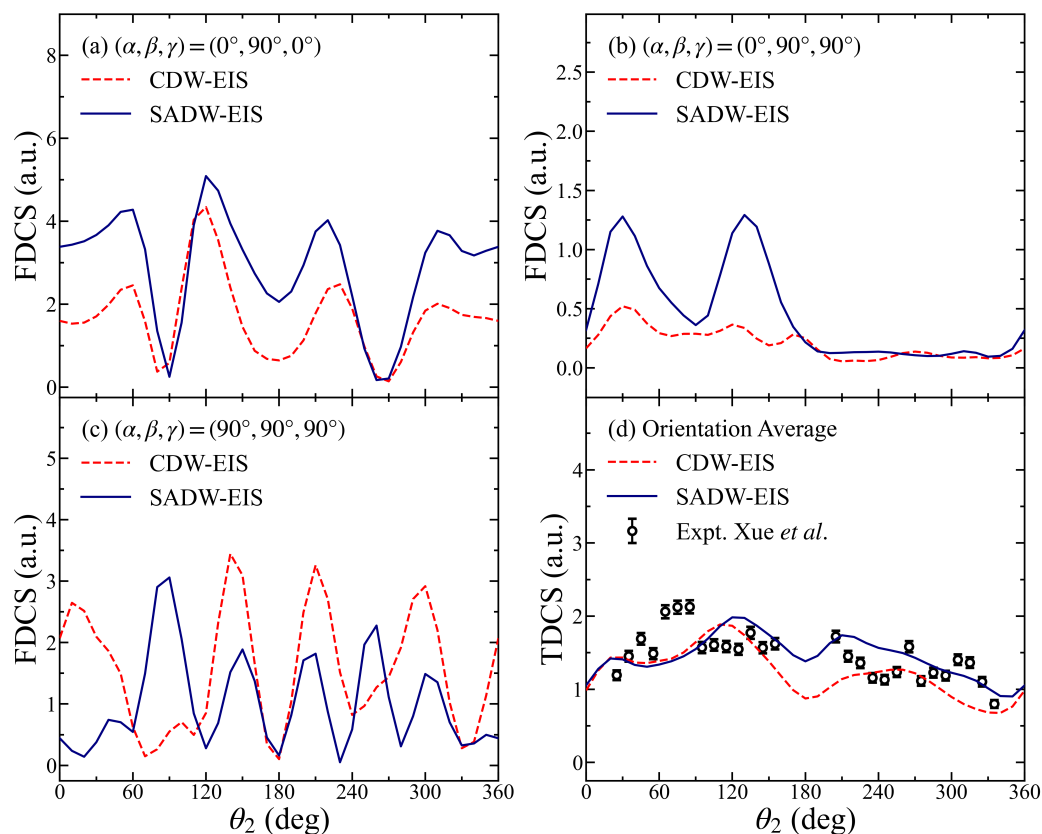


Figure 6. The same as Figure 3 for the single ionization of THF by 250 eV electron impact. Experimental data obtained from Ref. [16].

In Figure 6d we benchmark the TDCS obtained after averaging over all orientations with recent measurements from Ref. [16]. The number of orientations that need to be considered to achieve convergence in this case is 1584. There, we observe that the experimental data do not clearly resolve the binary and recoil structures. The CDW-EIS and SADW-EIS models predict a two-peak binary structure, but seem to fail to reproduce a third peak suggested by the experiment at around 75° . Regarding the recoil region, the latter method improves the description of the recoil/binary relative magnitude, in contrast to the former model. In addition, the CDW-EIS method predicts a single broad recoil peak, whereas the SADW-EIS model suggests a series of local maxima, with decreasing magnitude as the secondary electron emission angle increases, which seems to be more in agreement with the experiment.

To summarize, in this work we have theoretically studied electron-impact ionization of H_2O and THF at the fully differential level. Present results suggest that as the molecular complexity increases, non-oriented triple differential cross sections do not directly reflect the structures present in those obtained at particular orientations. This makes the task of performing an extensive averaging procedure unavoidable. Finally, we note that the results obtained by using two different representations for the molecular ion–electron interaction

show differences that survive to this averaging procedure, thus indicating that non-oriented triple differential cross sections can be used to benchmark models in an overall way.

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