Theoretical triple-differential cross sections of a methane molecule by a proper-average method

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For the last few years, our group has calculated cross sections for electron-impact ionization of molecules using the molecular three-body distorted-wave approximation coupled with the orientation-averaged molecular orbital (OAMO) approximation. This approximation was very successful for calculating ionization cross sections for hydrogen molecules and to a lesser extent nitrogen molecules. Recently we used the approximation to calculate single ionization cross sections for the $1t_2$ state of methane (CH_4) and we found major discrepancies with the experimental data. Here we investigate the validity of the OAMO approximation by calculating cross sections that have been properly averaged over all molecular orientations. These calculations with proper averages are in much better agreement with experiment than the OAMO calculations.

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I. INTRODUCTION

In fundamental physics, one of the most important unsolved problems is the few-body problem where we have to deal with more than two particles. Since we cannot solve the Schrödinger equation analytically for more than two particles, we have to use approximations for the theoretical models whose validity can only be checked by comparing with the experiments. One of the ways to study the few-body problem is through electron-impact ionization of atoms or molecules.

The study of electron-impact single ionization of atoms has provided valuable information about fundamental collisions for decades. More recently, molecules are starting to receive significant attention, at least partially due to the fact that there are potentially significant applications. For example, studies of the electron-impact ionization of biomolecules provide important information on the role of electrons in causing damage to DNA in biological systems. It is now well established that low-energy secondary electrons produced by high-energy primary radiation are responsible for much of the damage to DNA in living tissues [1,2]. The most detailed information about ionizing collisions between an electron and molecule is obtained from the triple-differential cross sections (TDCS) in which the energy and momentum of all three final-state particles are determined. The molecular three-body distorted-wave (M3DW) approximation has been one of the most successful theories for calculating TDCS for molecules.

Most of the experimentally measured TDCS for electron-impact ionization of molecules do not determine the orientation of the molecule so theory needs to average over all possible orientations to compare with experimental data. When we started performing M3DW calculations for molecules, we only had access to single processor computers and it was estimated that one calculation performing a proper average (PA) over orientations would take one to two years, depending on the size of the molecule. Since this was obviously not a practical possibility, we introduced the orientation-averaged molecular orbital approximation (OAMO) for the M3DW [3]. In the OAMO approximation, instead of averaging over orientation-dependent cross sections, the orientation-dependent molecular orbitals are averaged to obtain a spherically symmetric molecular orbital to use in the cross-section calculation. This average is performed once per molecule independent of the kinematics of the collision. Using this approximation, we found very good agreement with experimental data for ionization of the H_2 molecule [4–7] and reasonable agreement with the data for ionization of N_2 [8]. We extended the OAMO approach to compare with experimental data for ionization of the methane molecule (the simplest hydrocarbon). We examined ionization of the $1t_2$ and $2a_1$ states of methane, which have p-like and s-like characteristics, respectively. While the OAMO results were in relatively good agreement with experimental data for the low-energy symmetric scattering plane [9], there were some significant discrepancies with data for the asymmetric scattering plane calculations [10]. For the perpendicular plane, Al-Hagan *et al.* [11] predicted that if a molecule has a nucleus at the center of mass (c.m.), the cross sections in the perpendicular plane should exhibit a three-peak structure. Since methane has a nucleus at the c.m., a three-peak structure was expected. However, the experimental data exhibited a two-peak structure [10,12].

To better understand the methane results, we examined the isoelectronic targets (CH_4, NH_3, and Ne) [9,10,12,13]. The CH_4 molecule $1t_2$ state and NH_3 molecule $3a_1$ and $1e_1$ states all have p-like characteristics, whereas the CH_4 molecule $1a_1$ state and the NH_3 molecule $2a_1$ state have s-like characteristics. However, both the p-like and s-like states in CH_4 and NH_3 exhibited similar trends for the theoretical cross sections. This result may be caused by the orientation average approximation since, in the OAMO calculations, we are integrating wave function over orientations, which may change p-type structure into a spherical shape.

Xu *et al.* [10] compared experiment with the M3DW for electron-impact ionization of methane. They looked at asymmetric scattering both in the scattering plane and the perpendicular plane. They found that the agreement between the theory and experiment was not good, particularly in the perpendicular plane. Although the agreement with experiment was a little better in the scattering plane, it was still far from good. With increasing projectile scattering angle, the relative size of the experimental recoil peak became larger, whereas

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the theoretical intensity of the recoil peak decreased. The fact that the recoil peak is weaker than experiment suggests that nuclear scattering is underestimated in the theoretical model. Toth *et al.* [14] and Senftleben *et al.* [15] suggested that one way to increase the strength of the nuclear scattering is to move the nuclei closer to the c.m.. To check this idea, we did some test calculations in which we moved the H nuclei closer to the c.m., and we did observe a better agreement with experiment in the recoil region, which suggests that the OAMO approximation is underestimating the strength of the nuclear scattering.

In this paper, we report the results of a M3DW calculation for which a proper average over molecular orientations is performed. Our PA calculations are in much better agreement with the experimental data for CH_4 than the OAMO results. We have been using the Ward-Macek (WM) approximation [16] for the final-state interaction between the outgoing electrons [postcollision interaction (PCI)] since it gave better agreement with experimental data for the H_2 molecule than the exact Columbic interaction [16]. We tested the two methods for including PCI for the proper-average calculations, and we found that the results obtained using the exact Coulomb interaction (PA-Ex) were in better agreement with experiment than those obtained using the WM approximation (PA-WM).

II. THEORY

The molecular three-body distorted-wave (M3DW) approximation has been presented in previous publications [3–17] so only a brief outline of the theory will be presented. The TDCS for the M3DW is given by

$$\frac{d\sigma}{d\Omega_a d\Omega_b dE_b} = \frac{1}{(2\pi)^5} \frac{k_a k_b}{k_i} (|T_{\text{dir}}|^2 + |T_{\text{exc}}|^2 + |T_{\text{dir}} - T_{\text{exc}}|^2), \quad (1)$$

where $\vec{k}_i$, $\vec{k}_a$, and $\vec{k}_b$ are the wave vectors for the initial, scattered, and ejected electrons, T_{dir} is the direct scattering amplitude, and T_{exc} is the exchange amplitude. The direct scattering amplitude is given by

$$T_{\text{dir}} = \langle \chi_a^-(\vec{k}_a, \mathbf{r}_1) \chi_b^-(\vec{k}_b, \mathbf{r}_2) C_{\text{scat-eject}}(r_{12}) \times |V - U_i| \phi_{\text{Dy}}(\mathbf{R}, \mathbf{r}_2) \chi_i^+(\vec{k}_i, \mathbf{r}_1) \rangle, \quad (2)$$

where r_1 and r_2 are the coordinates of the incident and the bound electrons; χ_i, χ_a, and χ_b are the distorted waves for the incident, scattered, and ejected electrons, respectively; $\phi_{\text{Dy}}(\mathbf{R}, \mathbf{r}_2)$ is the initial bound-state Dyson molecular orbital; and $\mathbf{R}$ is the orientation of the molecule. In the OAMO approximation, $\phi_{\text{Dy}}(\mathbf{R}, \mathbf{r}_2)$ is replaced with $\phi_{\text{Dy}}^{\text{OA}}(r_2)$, which is the molecular orbital averaged over all orientations $\mathbf{R}$. In M3DW-OAMO calculations, we average all orientations for the molecular orbital once independent of the kinematics of the collision and then we find TDCS with a single calculation of the T matrix. In the proper-average calculations, we find the TDCS for each orientation and then we average over all orientations. The molecular wave functions were calculated using density functional theory along with the standard hybrid B3LYP [18] functional by means of the ADF 2007 (Amsterdam density functional) program [19] with the triple-ζ with two polarization functions Slater-type basis sets.

The factor $C_{\text{scat-eject}}(r_{12})$ is the final-state Coulomb interaction between the two outgoing electrons (PCI). We have been using the WM average Coulomb-distortion factor between the two final-state electrons [16] since it gave good agreement with experiment for ionization of H_2 (using the OAMO approximation). In this work, we compare the results obtained using the WM approximation with results obtained using the exact Coulomb interaction.

The remaining undefined symbols used in the T matrix are V, which is the initial-state interaction potential between the incident electron and the neutral molecule, and U_i, which is a spherically symmetric initial-state distorting potential which is used to calculate the initial-state distorted wave for the incident electron $\chi_i^+(\vec{k}_i, \mathbf{r}_1)$.

Details about the calculation of initial- and final-state distorted waves can be found in Madison and Al-Hagan [20]. For the exchange amplitude, particles 1 and 2 are interchanged in the final-state wave function in Eq. (2) [12].

III. RESULTS AND DISCUSSION

A. Accuracy of proper-average calculations

Since we have found good agreement between experiment and the M3DW for ionization of H_2 using the OAMO approximation, the first question that we wanted to address concerns the accuracy of the OAMO approximation for H_2. Figure 1 contains a comparison between H_2 results calculated using the OAMO approximation and with proper averages for scattering into the perpendicular plane with both final-state electrons having the same energy and a relatively low incident electron energy of 54 eV, which is in the energy range of several recent experiments. The largest difference between the two
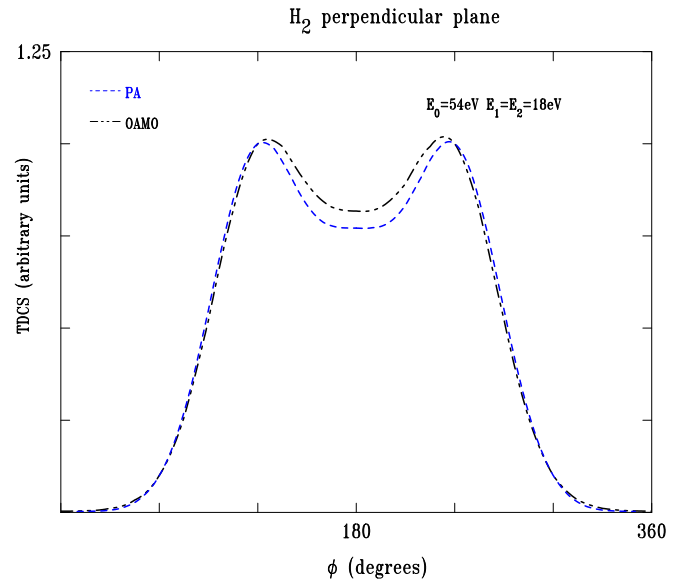

FIG. 1. (Color online) Triple-differential cross sections as a function of ejected electron angle for 54 eV electron-impact ionization of H_2 in the perpendicular plane. Projectile scattering angle is 50°. Both scattered and ejected electrons have an energy of 18 eV. The one long, two short-dashed curves are M3DW-OAMO calculations and the dashed curves are PA calculations for the M3DW.

calculations is 5% at 180° which is smaller than experimental error. We have tried other cases with similar kinematics and found analogous results, so we conclude that the OAMO approximation is valid for H_2 at least for these kinematics. Of course, this is to be expected since we have shown the validity of the OAMO approximation for H_2 previously using an analytic approximation for the ground-state wave function (13). Consequently, we conclude that the good agreement we have achieved for H_2 using the OAMO approximation is not fortuitous. We were also pleasantly surprised to find that we could get converged averages for H_2 using only 25 different orientations.

B. Proper-average calculations of methane

Next we compared theoretical OAMO and PA cross sections for electron-impact ionization of the $1t_2$ state of methane with
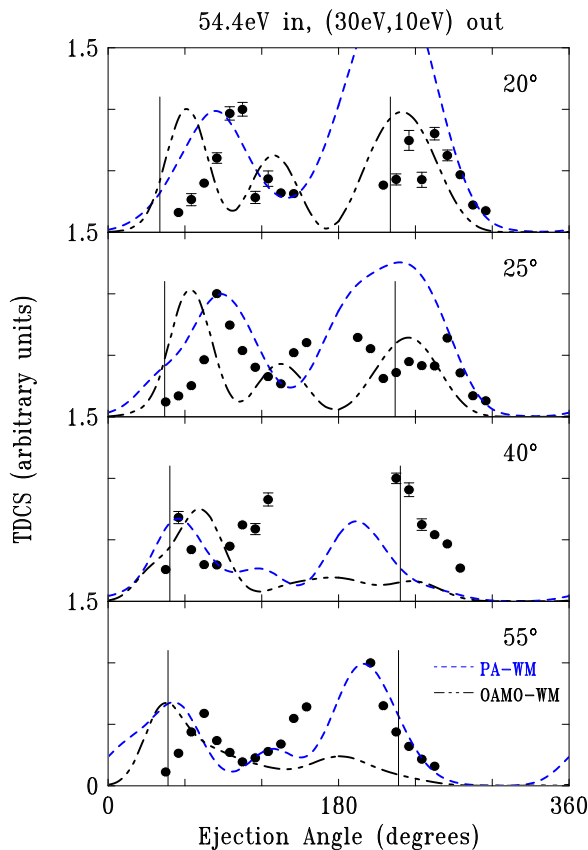

FIG. 2. (Color online) TDCS for 54.4 eV electron-impact ionization of the $1t_2$ state of methane in the scattering plane. The horizontal axis is the ejected (slower final-state) electron detection angle. The energy of the scattered electron (faster final-state electron) is 30 eV and the energy of the ejected electron is 10 eV. Results are presented for projectile scattering angles ranging between 20° (top) and 55° (bottom). The solid vertical line in the small angular range corresponds to the classical momentum transfer direction. The solid vertical line for large angles corresponds to the classical momentum transfer direction plus 180°. Circles are the experimental data of Xu *et al.* [10], one long, two short-dashed lines are M3DW-OAMO calculations, and dashed lines are M3DW PA calculations. The WM approximation for PCI was used for both theoretical curves.

experimental data for 54.4 eV incident electron energy. The ionization energy of the $1t_2$ state is 14.4 eV, and we assume that the energy of the recoil ion is negligible. Consequently, from energy conservation, the rest of the energy (40 eV) is shared by the scattered and ejected electrons. We examined different sets of energy for the scattered and ejected electrons and for different fixed scattering angles for the fast electrons from 15° to 55°. The experimental data had been measured by Alexander Dorn's group at Heidelberg, Germany, for both coplanar and perpendicular plane geometry.

C. Coplanar geometry

If the ejected electrons are detected in the scattering plane (plane determined by the incident and faster final-state electron wave vectors), the process is called coplanar geometry. In Fig. 2, experimental and theoretical results are presented for the case where the scattered and ejected electron energies have energies of 30 and 10 eV, respectively. Cross sections are presented for four different projectile (faster final-state electron) scattering angles ranging between 20° and 55°. For each figure, the experimental data are normalized to the unity for the largest cross section and the theoretical results are normalized to the best visual fit to the data. All of the theoretical results were obtained using the WM approximation for PCI.

Conventionally, the angular distributions are divided into two regions. These are the angular region between 0° and 180°,
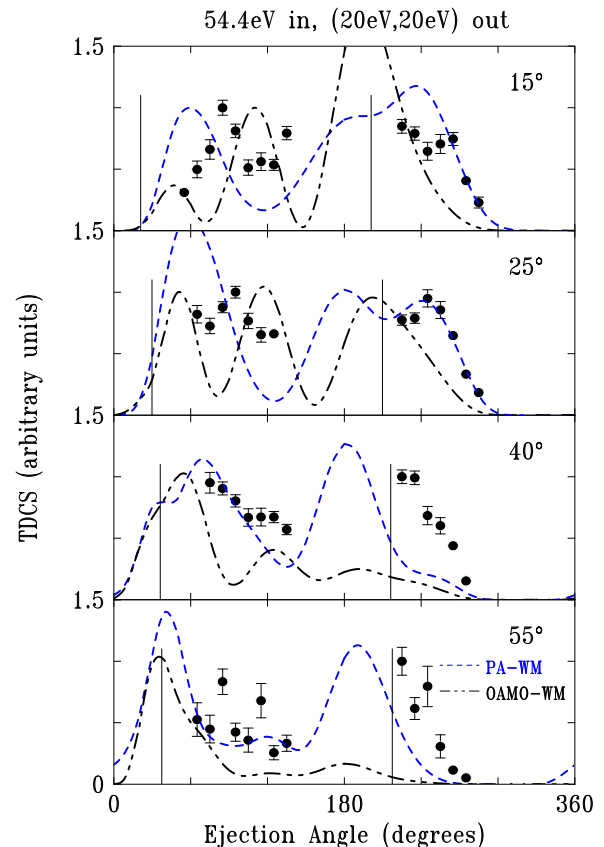

FIG. 3. (Color online) Same as Fig. 2 except that both final-state electrons have an energy of 20 eV.

which is known as the binary region, and the region between 180° and 360°, which is called the recoil region [21]. Typically, the angular distributions have one peak in the binary region located near the momentum transfer direction (left vertical line in the figure) and this peak is attributed to a binary collision between the projectile and target electrons. In the recoil region, there is normally also one peak (generally much smaller than the binary peak) and this peak is normally located near the momentum transfer direction plus 180° (right vertical line in the figure). This peak is attributed to a double collision mechanism where the first collision is the binary collision ejecting the electron in the momentum transfer direction. However, as the electron leaves the target, there is a second collision with the attractive nuclei which backscatters the electron by 180°. From Fig. 2, it is seen that the recoil peak is larger than the binary peak for the larger projectile scattering angles and that the peak location for both the binary and recoil peaks are significantly shifted from the vertical lines. The OAMO calculations have a split in a binary peak for projectile scattering angles of 20° and 25°, which is not uncommon for atomic *p* states. However, the experimental data does not appear to have a split binary peak.

Our PA calculations exhibited better agreement with the experimental data than the OAMO results. For the binary region, the PA did not predict a split binary peak in accordance with experiment and the binary peak locations were also closer to the data. For the recoil peak, the experimental data shows the

relative intensity of the recoil peak to increase with increasing projectile scattering angle. Whereas the OAMO predicted that the intensity will decrease, our PA calculations predicted recoil peaks in better accord with the experimental data.

Figure 3 contains results similar to Fig. 2 except that the scattered and ejected electron energies are both 20 eV. OAMO calculations again predict a broad split in the binary peak region for the three smallest projectile scattering angles and relative recoil peak intensities much smaller than experiment for the two largest projectile scattering angles. The PA calculations are again in much better agreement with experimental data in general, and in particular, the relative magnitudes of the binary and recoil are much better than the OAMO results.

D. Perpendicular geometry

As mentioned in the Introduction, Al-Hagan *et al.* [7] predicted that one should expect three peaks (two elastic scattering and one nuclear scattering) for electron-impact ionization of molecules that have a nucleus at the c.m., which is the case for methane. The published OAMO calculations exhibited a three-peak structure for the perpendicular plane for both symmetric and asymmetric energy sharing [10,12]. Figure 4 contains a comparison between experiment and theory in the perpendicular plane for the asymmetric energy sharing case. As before, the experimental data is normalized to unity and the theoretical calculations are normalized for a
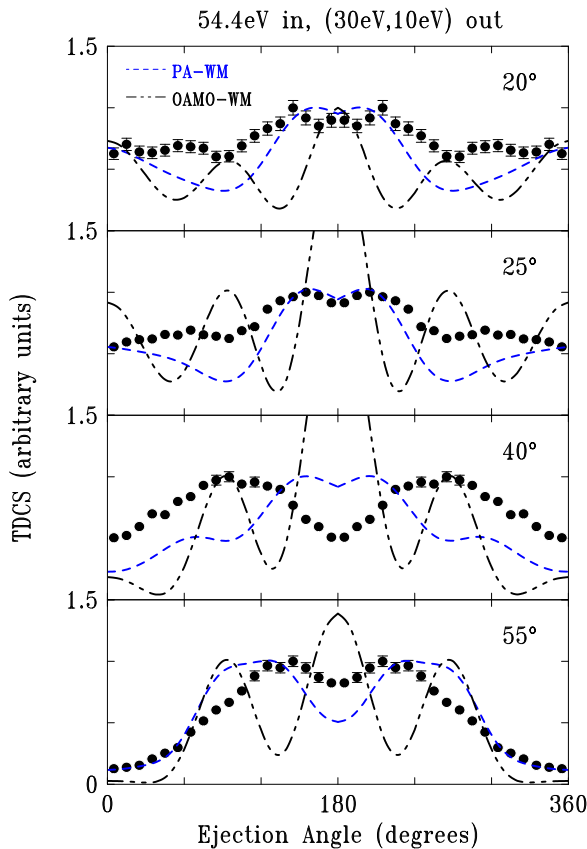

FIG. 4. (Color online) Same as Fig. 2 except for the perpendicular plane.
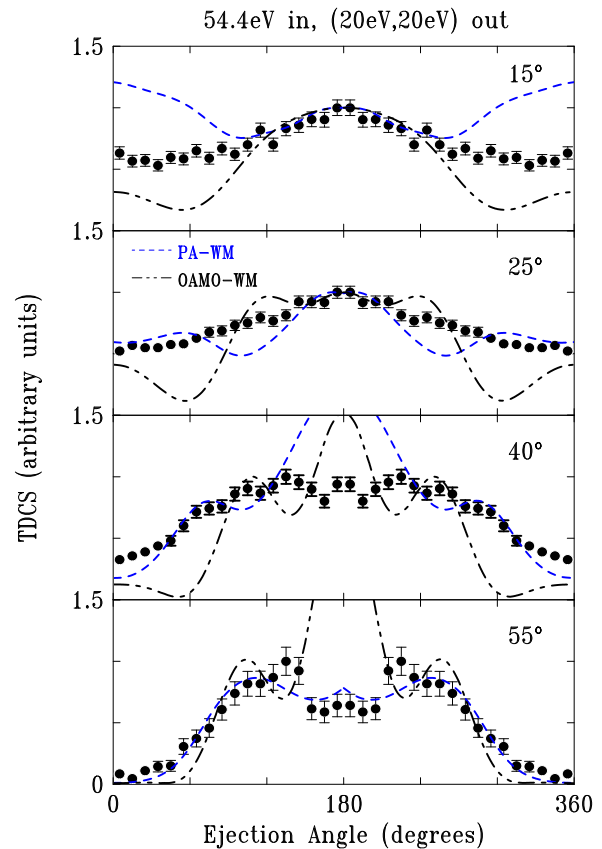

FIG. 5. (Color online) Same as Fig. 3 except for the perpendicular plane.

best visual fit to the experimental data. Instead of having a maximum at 180° as predicted by the OAMO approximation, the experimental data has a local minimum and the PA calculations also have a 180° minimum in accordance with experiment. Overall, the PA calculations are in reasonably good qualitative agreement with the experimental data. The most significant disagreement between experiment and theory occurs at a projectile scattering angle of 40° where the 180° experimental dip is smaller than the theoretical, and 55° where the theoretical dip is smaller.

Figure 5 presents the same comparison as Fig. 4, except that the two final-state electrons both have the same energy of 20 eV. For this case, the OAMO results only have a single peak at 180° in accordance with experiment for the smallest projectile scattering angle of 15°. For the three larger projectile scattering angles, the OAMO results have the expected three peaks. The experiment, on the other hand, exhibits a (small) 180° peak for all projectile scattering angles with a single peak for the two smaller angles and three peaks for the two larger projectile scattering angles. The PA calculations are in qualitative agreement with experiment for all four projectile scattering angles with the biggest disagreement with experiment occurring for projectile scattering angles of 15° (small and large ejection angles) and 40° (180° peak too large).

E. Postcollision interaction

In the final channel, there is a Columbic interaction between the two outgoing electrons (PCI). In distorted-wave Born approximation calculations, this interaction can be either approximated by the WM approximation [16] or the Columb interaction can be treated exactly. The WM approximation (or a variant) has been very popular since it can be used in a distorted-wave calculation with essentially no additional work. To use the exact interaction is much more difficult [19]. However, since we do everything numerically, there is no time savings for us to use the WM approximation. However, we have been using it since we found that, for ionization of H_2 (and using the OAMO approximation), the WM approximation consistently gave better agreement with experiment than using the exact full Coulomb interaction [16]. This always seemed a bit odd to us so we decided to test it again for our PA calculations.

Figure 6 contains a comparison of M3DW results properly averaged over orientations and with PCI treated either using the WM approximation or using the proper Columbic interaction for coplanar asymmetric scattering (same as Fig. 2). From the figure, it is seen that the two different treatments of PCI give similar results except for a projectile scattering angle of 40° where there was a big change in the recoil region with the exact PCI treatment giving results in much better agreement with experimental data. For the other three projectile scattering angles, it is difficult to claim that one is better than the other. Figure 7 contains the same comparison except for equal energy
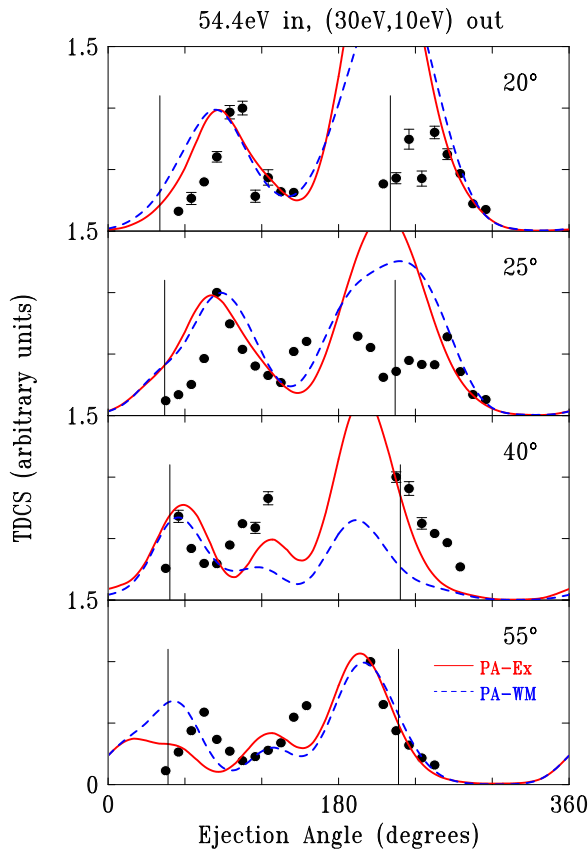

FIG. 6. (Color online) Same as Fig. 2 except that both theoretical calculations are M3DW with PAs over orientations with different treatments of PCI. For the dashed curve, the WM approximation is used for PCI; and for the solid curve, the full exact Coulomb interaction is used for PCI.
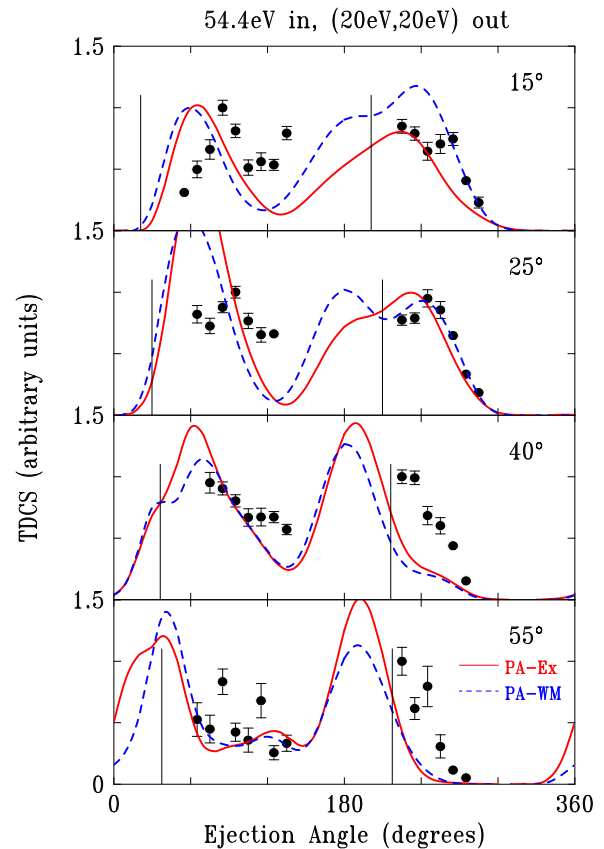

FIG. 7. (Color online) Same as Fig. 6 except that both final-state electrons have an energy of 20 eV.
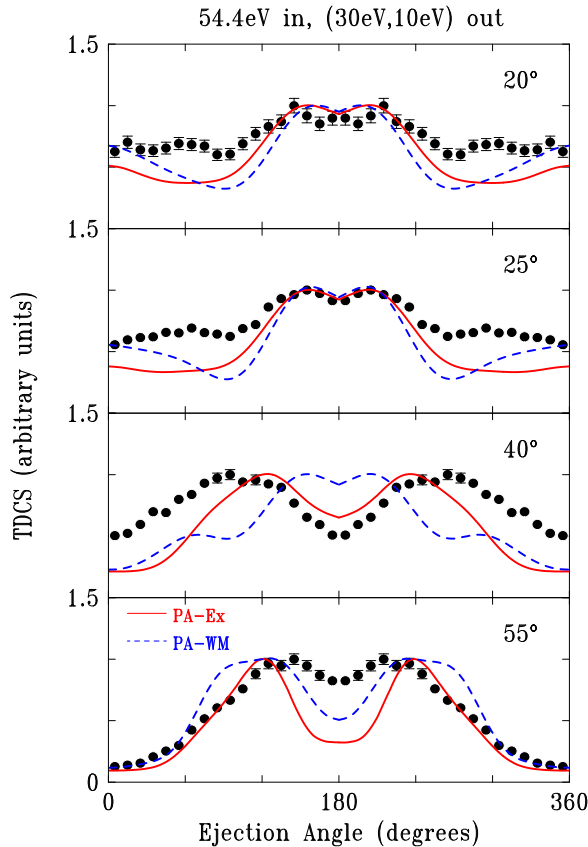
FIG. 8. (Color online) Same as Fig. 6 except for the perpendicular plane.

FIG. 9. (Color online) Same as Fig. 7 except for the perpendicular plane.

final-state electrons. In this case, there is not much difference for all projectile scattering angles and it is difficult to claim that one is better than the other.

Figures 8 and 9 contain M3DW results properly averaged over orientations and with PCI treated either using the WM approximation or using the proper Columbic interaction for perpendicular plane scattering (same as Figs 4 and 5). For the perpendicular plane, the full exact treatment of exchange clearly results in much better agreement with experiment. The most dramatic case is for a scattering angle of 40° and equal energy electrons where the peak at 180° becomes a shallow minimum in agreement with experiment. The worst agreement with experiment was found for unequal electron energies and the largest projectile scattering angle of 55° where the 180° minimum was significantly deeper than the experimental one. However, the overall agreement between experiment and PA exact PCI M3DW results was very good for all the perpendicular plane measurements.

IV. CONCLUSIONS

We have presented PA M3DW calculations for (*e*,2*e*) ionization of molecules. We had previously shown that the OAMO approximation should be valid for H_2 by using analytic wave functions for the ground state (13) and we verified that the OAMO and properly averaged results were the same to within experimental error for 54 eV incident electrons and equal energy final-state electrons, which is the energy range of
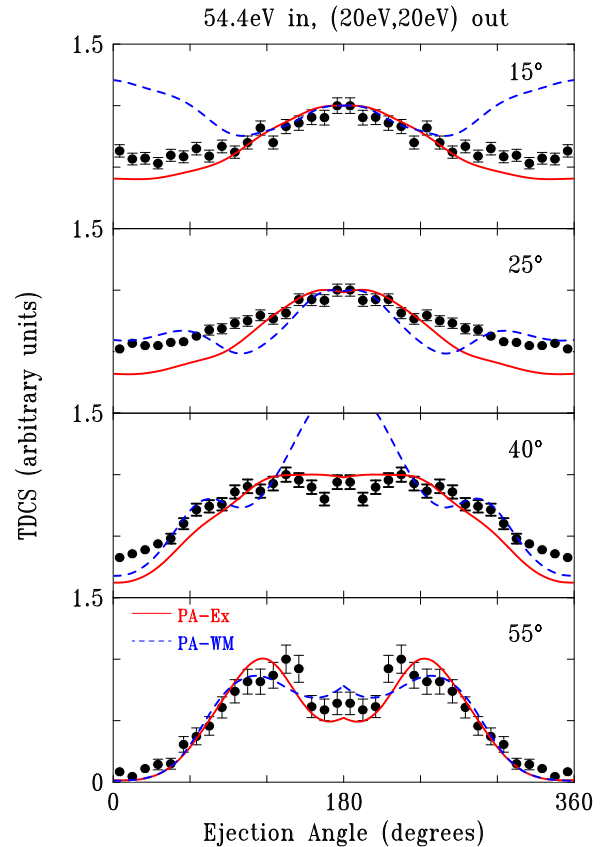
many of the recent experiments. We then calculated the TDCS for (*e*,2*e*) ionization of the $1t_2$ molecular state of methane. A comparison was made between the experimental data, OAMO calculations, and PA calculations for coplanar and perpendicular plane scattering. The PA calculations were in much better agreement with experimental data than the OAMO calculations. For coplanar scattering, the PA calculations did a better job of predicting the number and location of binary peaks and they were also in much better agreement with experiment for the recoil peak. However, the most dramatic improvement occurred for the perpendicular plane where the OAMO approximation normally predicted three peaks with one peak at 180° electron ejection angle, whereas experiment predicted a minimum for most cases. The PA calculations, on the other hand, properly predicted the number of peaks for all cases except one and qualitatively predicted the shape of the experimental data.

We also tested the treatment of PCI. We had previously found for H_2 using the OAMO approximation, that the WM [16] yielded better agreement with experiment than the full exact treatment of PCI. We performed M3DW PA calculations treating PCI either with the WM approximation or with the full exact Coulomb interaction. For coplanar scattering, there was not much difference between exact PCI and WM except for one case where the exact treatment clearly predicted a better recoil peak. For the perpendicular plane, on the other hand, the exact treatment yielded better agreement with experiment for all cases (some more dramatic than others) and the

exact treatment results are in fairly good agreement with all the perpendicular plane measurements (better than the coplanar).

[1] B. Boudaïffa, Science **287**, 1658 (2000).

[2] F. Martin, P. D. Burrow, Z. Cai, P. Cloutier, D. Hunting, and L. Sanche, Phys. Rev. Lett. **93**, 068101 (2004).

[3] J. Gao, J. L. Peacher, and D. H. Madison, J. Chem. Phys. **123**, 204302 (2005).

[4] J. Gao, D. H. Madison, and J. L. Peacher, J. Phys. B: At., Mol. Opt. Phys. **39**, 1275 (2006).

[5] J. Gao, D. H. Madison, J. L. Peacher, A. J. Murray, and M. J. Hussey, J. Chem. Phys. **124**, 194306 (2006).

[6] D. S. Milne-Brownlie, M. Foster, J. Gao, B. Lohmann, and D. H. Madison, Phys. Rev. Lett. **96**, 233201 (2006).

[7] Z. N. Ozer, H. Chaluvadi, M. Ulu, M. Dogan, B. Aktas, and D. Madison, Phys. Rev. A **87**, 042704 (2013).

[8] A. J. Murray, M. J. Hussey, J. Gao, and D. H. Madison, J. Phys. B: At., Mol. Opt. Phys. **39**, 3945 (2006).

[9] K. L. Nixon, A. J. Murray, H. Chaluvadi, C. Ning, and D. H. Madison, J. Chem. Phys. **134**, 174304 (2011).

[10] S. Xu, H. Chaluvadi, X. Ren, T. Pflüger, A. Senftleben, C. G. Ning, S. Yan, P. Zhang, J. Yang, X. Ma, J. Ullrich, D. H. Madison, and A. Dorn, J. Chem. Phys. **137**, 024301 (2012).

[11] O. Al-Hagan, C. Kaiser, D. Madison, and A. J. Murray, Nat. Phys. **5**, 59 (2008).

[12] K. L. Nixon, A. J. Murray, H. Chaluvadi, S. Amami, D. H. Madison, and C. Ning, J. Chem. Phys. **136**, 094302 (2012).

[13] K. L. Nixon, A. J. Murray, H. Chaluvadi, C. Ning, J. Colgan, and D. H. Madison, J. Chem. Phys. **138**, 174304 (2013).

[14] I. Tóth and L. Nagy, J. Phys. B: At., Mol. Opt. Phys. **43**, 135204 (2010).

[15] A. Senftleben, T. Pflüger, X. Ren, B. Najjari, A. Dorn, and J. Ullrich, J. Phys. B: At., Mol. Opt. Phys. **45**, 021001 (2012).

[16] S. J. Ward and J. H. Macek, Phys. Rev. A **49**, 1049 (1994).

[17] J. Gao, D. H. Madison, and J. L. Peacher, Phys. Rev. A **72**, 032721 (2005).

[18] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[19] C. F. Guerra, J. G. Snijders, G. Velde, and E. J. Baerends, Theor. Chem. Acc. **99**, 391 (1998).

[20] D. H. Madison and O. Al-Hagan, J. At., Mol., Opt. Phys. **2010**, 367180 (2010).

[21] J. D. Builth-Williams, S. M. Bellm, D. B. Jones, H. Chaluvadi, D. H. Madison, C. G. Ning, B. Lohmann, and M. J. Brunger, J. Chem. Phys. **136**, 024304 (2012).

[22] C. Catlett *et al.*, in *HPC and Grids in Action*, edited by Luco Grandinetti (IOS Press, Amsterdam, 2007).