Single ionization of CH₄ by bare ions: Fully differential cross sections

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A theoretical study of fully differential cross sections for the single ionization of CH_4 by collisions with H^+, He^{2+}, and C^{6+} ions at energies in the order of MeV/amu is presented. We work in terms of the Born-3DW model, which considers a non-Coulomb central potential for the interaction of the active electron with the molecular core. Results obtained with the Born-3DW model are compared to those obtained with the Born-C3 model, which assumes this potential as purely Coulombic. The anisotropic potential of the CH_4 molecule is smoothed through an angular integration, and results are averaged over all the possible orientations of the target molecule. Results for the lesser bound molecular orbitals ($1T$ and $2A_1$) are presented and discussed for different projectile momentum transfers for the coplanar geometry.

PACS number(s): 34.10.+x, 34.50.Fa, 52.20.Hv

I. INTRODUCTION

Ionization of atoms and molecules by fast charged particles has been a matter of active research in the last two decades [1], and it is nowadays a well-documented subject with relevance in many areas like atmosphere, (fusion) plasma physics, or astrophysics. In addition, it has been checked that ionization cross sections for biological molecules are quite useful in medical studies, like radiobiology, medical imaging, and radiotherapy [2].

Since the mid-1990s, the Cold Target Recoil Ion Momentum Spectroscopy (COLTRIMS) [3–5] technique has provided a kinematically complete insight of collision processes involving photons, ions, and electrons [6–9]. Following the Frankfurt and Heidelberg groups this technique has since then been adopted by several laboratories worldwide. Despite the limitations in the experimental setup (only low-energy emitted electrons are detected to avoid prohibitive extraction fields), a vast amount of data has been obtained for a large variety of collision systems. More recent works have been realized in ion-atom [10–12], ion-molecule [13–16], and ion-cluster [17] collisions.

Theoretically, Fully Differential Cross Sections (FDCS) in ion-atom collisions have been calculated to describe the existing data in terms of continuum distorted waves methods [18–23] or using the classical trajectory Monte Carlo method (CTMC) [24–26].

In this work we consider the single ionization of the methane molecule by fully stripped ions at high-impact energies. Motivation for the present analysis is provided by the need of ionization cross sections of methane in fields like astrophysics (planetary atmospheres studies), in radiobiology, where the methane molecule resembles organic matter, or in fusion plasmas, where carbon atoms can be ejected from the fist wall and react with the hydrogen forming methane and other hydrocarbons in the cold zones of the plasma, like the divertors.

The present paper is organized as follows. In Sec. II we describe in detail the theoretical model employed to calculate the FDCS which is based on a Born-type initial-state and a final-state wavefunction built upon three distorted waves

(Born-3DW model). For the electron-core interaction we use a central model potential that we build upon the orbitals provided by Moccia [27] as one-center expansions in terms of Slater functions. Although a particular case of the Born-3DW model, we hereafter refer as the Born-C3 model to the case in which the electron-core interaction in the final state is represented by a pure Coulomb potential leading to the well-known C3 function [28,29]. In Sec. IV we present and discuss our results. We compare the angular distributions obtained with the Born-3DW and the simpler Born-C3 model for different emission energies and transferred momenta. In Sec. V, we draw the main conclusions and summarize the perspectives of our work.

Atomic units are used throughout this work unless otherwise indicated.

II. THEORY

A. Born-3DW approximation

We consider a stripped ion of charge Z_P and mass M_P incident upon a multielectron molecular target of mass M_T in the ground state. According to the independent particle model (IPM), we consider one active electron placed in the molecular orbital i of the ground state, so the target initial wavefunction can be written as $\phi_i(\mathbf{r})$, eigenfunction of the molecular model potential $V_{\text{mol}i}(\mathbf{r})$, that includes the nuclei and the other electron terms:

$$V_{\text{mol}i}(\mathbf{r}) = -\sum_{l=1}^{M} \frac{Z_l}{|\mathbf{r} - \mathbf{R}_l|} + \sum_{j=1}^{N_{MO}} N_{ij} \int d^3\mathbf{r}' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where M is the number of nuclei which form the molecule, Z_l the charge of each nuclei, $\mathbf{R}_l$ their position with respect to the molecular center of mass, N_{MO} the number of molecular orbitals of the molecule, N_{ij} values 2 if $i \neq j$ and 1 if $i = j$, and $\phi_j(\mathbf{r}')$ their one-electron wavefunctions. In our case, the wavefunctions for CH_4 are taken from [27], where they are expanded in a Slater functions basis set as follows:

$$\phi_i(\mathbf{r}) = \sum_{j=1}^{n} a_{ij} \, \mathcal{R}_{n_{ij} l_{ij} \xi_{ij}}(r) \, Y_{l_{ij} m_{ij}}(\hat{\mathbf{r}}), \quad (2)$$

where $Y_{l_{ij}m_{ij}}(\hat{\boldsymbol{r}})$ are the spherical harmonics and $\mathcal{R}_{n_{ij}l_{ij}\xi_{ij}}(r)$ Slater type functions given by

$$\mathcal{R}_{n_{ij}l_{ij}\xi_{ij}}(r) = \sqrt{\frac{(2\xi_{ij})^{2n_{ij}+1}}{(2n_{ij})!}} \, e^{-\xi_{ij}r} \, r^{n_{ij}-1}. \qquad (3)$$

Although in [27] the coefficients a_{ij} are given in terms of the real spherical harmonics $C_{lm}(\hat{\boldsymbol{r}})$ and $S_{lm}(\hat{\boldsymbol{r}})$, the expansion can be written in the function of the complex spherical harmonics $Y_{lm}(\hat{\boldsymbol{r}})$ by introducing simple multiplication factors $\frac{1}{\sqrt{2}}$ and the imaginary unit i when $m \neq 0$:

$$m = 0 \quad C_{l0}(\hat{\boldsymbol{r}}) = Y_{l0}(\hat{\boldsymbol{r}}),$$

$$m > 0 \quad C_{lm}(\hat{\boldsymbol{r}}) = \frac{1}{\sqrt{2}} [Y_{lm}(\hat{\boldsymbol{r}}) + (-1)^m Y_{l-m}(\hat{\boldsymbol{r}})], \qquad (4)$$

$$m < 0 \quad S_{lm}(\hat{\boldsymbol{r}}) = \frac{1}{i\sqrt{2}} [Y_{lm}(\hat{\boldsymbol{r}}) - (-1)^m Y_{l-m}(\hat{\boldsymbol{r}})].$$

To carry out the following algebra, it is convenient to write the wavefunction (2) separating the radial and angular part as follows:

$$\phi_i(\boldsymbol{r}) = \sum_{lm} R_{ilm}(r) \, Y_{lm}(\hat{\boldsymbol{r}}), \qquad (5)$$

where the radial part R_{ilm} is, comparing with (2),

$$R_{ilm}(r) = \sum_j a_{ij} \, \mathcal{R}_{n_{ij}l_{ij}\xi_{ij}}(r), \qquad (6)$$

extending the sum for all j that $l_{ij} = l$ and $m_{ij} = m$.

As $\boldsymbol{K}_i$ is the initial incident momentum of the impacting projectile, $\boldsymbol{K}_f$ the momentum of the scattered projectile after the collision, and $\boldsymbol{k}$ the momentum of the ionized electron, the fully differential cross section is given by [30]

$$\frac{d^5\sigma}{d^2\boldsymbol{q}_\perp \, d^3\boldsymbol{k}} = (2\pi)^4 \, N_e \, \frac{\mu_{\mathrm{I}e}\mu_{\mathrm{PT}}^2}{K_i K_f} |T_{fi}|^2, \qquad (7)$$

where $\boldsymbol{q}$ is the momentum transferred by the projectile,

$$\boldsymbol{q} = \boldsymbol{K}_i - \boldsymbol{K}_f, \qquad (8)$$

$\boldsymbol{q}_\perp$ denotes its component perpendicular to $\boldsymbol{K}_i$, N_e the number of electrons in the molecular orbital i, and $\mu_{\mathrm{I}e}$, μ_{PT} are the relative reduced electron-target and projectile-target masses after the ionization takes place:

$$\mu_{\mathrm{I}e} = \frac{M_{\mathrm{I}}}{M_{\mathrm{I}}+1}, \qquad (9)$$

$$\mu_{\mathrm{PT}} = \frac{M_{\mathrm{P}}(M_{\mathrm{I}}+1)}{M_{\mathrm{P}}+M_{\mathrm{I}}+1}, \qquad (10)$$

with M_{P}, M_{I} the masses of the projectile and not-ionized target, respectively.

The transition amplitude for single ionization can be written as

$$T_{fi} = \langle \Psi_f \,|\, V_{\mathrm{I}} \,|\, \Psi_i \rangle, \qquad (11)$$

where the initial channel wavefunction $\Psi_i(\boldsymbol{K}_i; \boldsymbol{R}_i, \boldsymbol{r})$ is given by a bound wavefunction for the molecular orbital under consideration times an incident plane wave for the incoming projectile:

$$\Psi_i = \frac{1}{(2\pi)^{3/2}} e^{i\boldsymbol{K}_i \cdot \boldsymbol{R}_i} \phi_i(\boldsymbol{r}), \qquad (12)$$

where $\boldsymbol{R}_i$ is the relative coordinate between the projectile and the center of mass of the target molecule before the collision. The final channel wavefunction $\Psi_f(\boldsymbol{K}_f; \boldsymbol{R}_f, \boldsymbol{r})$ is written as

$$\Psi_f = \frac{1}{(2\pi)^{3/2}} e^{i\boldsymbol{K}_f \cdot \boldsymbol{R}_f} C^-(\boldsymbol{K}_f; \boldsymbol{R}_f)$$
$$\times \chi^-(\boldsymbol{k}; \boldsymbol{r}) C^-(\boldsymbol{k}_{e\mathrm{P}}; \boldsymbol{R}_f - \boldsymbol{r}), \qquad (13)$$

where $\boldsymbol{r}$ is the coordinate of the ejected electron with respect to the center of mass of the ionized target system, $\boldsymbol{R}_f$ the position of the projectile with respect to the same origin after the collision; $\chi^-(\boldsymbol{k}; \boldsymbol{r})$ represents a final continuum wavefunction $(E > 0)$ for the emitted electron with a determined momentum $\boldsymbol{k}$ subject to the potential $V_{\mathrm{mol}i}(\boldsymbol{r})$, and $C^-(\boldsymbol{K}_f, \boldsymbol{R}_f), C^-(\boldsymbol{k}_{e\mathrm{P}}, \boldsymbol{R}_f - \boldsymbol{r})$ are the Coulombian distortions for the internuclear interaction and the emitted electron-projectile subsystem, respectively. The interaction potential V_{I} is given by the nonresolved part of the Hamiltonian by the initial state:

$$V_{\mathrm{I}}(\boldsymbol{R}_i, \boldsymbol{r}) = -\frac{Z_{\mathrm{P}}}{|\boldsymbol{r} - \boldsymbol{R}_i|} - Z_{\mathrm{P}} \, V_{\mathrm{mol}i}(\boldsymbol{R}_i). \qquad (14)$$

As a first approximation, to calculate the continuum wavefunction of the ejected electron, we do not use the real anisotropic potential $V_{\mathrm{mol}i}(\boldsymbol{r})$ shown in (1). Instead, we use a radial $U_i(r)$ resulting from its angular integration:

$$U_i(r) = \frac{1}{4\pi} \int_{4\pi} d\Omega \, V_{\mathrm{mol}i}(\boldsymbol{r}). \qquad (15)$$

In Fig. 1, we show the potential $U_i(r)$ and compare it to the asymptotic Coulomb potential $-1/r$. Despite the averaging process, we note that the hydrogen atoms leave a clear trace in the potential through the minimum that can be seen about $r = 2.1$ a.u. Then the continuum wavefunction $\chi^-(\boldsymbol{k}; \boldsymbol{r})$ can be separated in a radial and angular part,

$$\chi^-(\boldsymbol{k}; \boldsymbol{r}) = \sum_{l=0}^\infty \sum_{m=-l}^{+l} \frac{4\pi}{kr} i^l \, {}^{-i\sigma_l} u_l(k; r) Y_{lm}^*(\hat{\boldsymbol{k}}) Y_{lm}(\hat{\boldsymbol{r}}), \qquad (16)$$

where $\sigma_l = \sigma_l^{\mathrm{Coul}} + \delta_l$, and $\sigma_l^{\mathrm{Coul}} = \arg[\Gamma(l+1+i\alpha)]$, δ_l is the non-Coulombic phase shift of the radial waves with respect
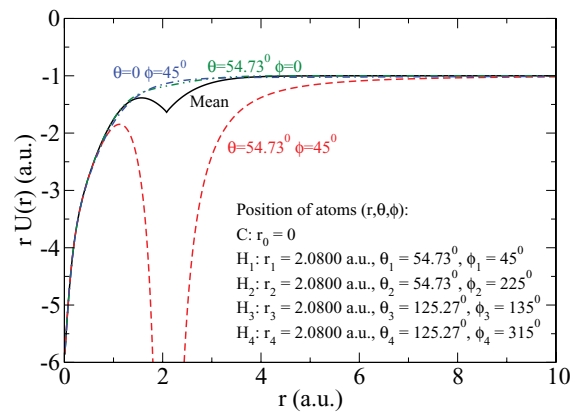

FIG. 1. (Color online) Radially integrated potential for orbital $1\mathrm{T}_{2z}$ of CH_4 molecule $U_{1\mathrm{T}_{2z}}(r)$, and some cuts of three-dimensional potential $V_{1\mathrm{T}_{2z}}(\boldsymbol{r})$.

to the Coulomb asymptotic ones [31], and $\alpha = -Z_{\rm T}/k$ is the Sommerfeld parameter for the asymptotic Coulomb problem. The radial wavefunction $u_l(k;r)$ fulfills the equation,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + U_i(r) \right] u_l(k;r) = \frac{k^2}{2} u_l(k;r). \tag{17}$$

We have employed Salvat's code throughout this work to obtain the $u_l(k;r)$ partial waves as well as the non-Coulombic phase shifts δ_l [32]. The transition amplitude $|T_{fi}|$ depends on the orientation of the target molecule through the electronic initial and final wavefunction $\phi_i(\mathbf{r})$, $\chi^-(\mathbf{k};\mathbf{r})$, and the second term of the interaction potential (14) $V_{\text{mol}i}(\mathbf{R})$. Hence, we obtain the transition amplitudes for a given orientation of the molecule, which, in the case where it involves more than two atoms, is characterized for the three Euler angles (α,β,γ) so we can define an octuple differential cross section as a function of these angles:

$$\frac{d^8\sigma}{d^2\mathbf{q}_\perp\, d^3\mathbf{k}\, d\alpha\, d\beta\, d\gamma} = (2\pi)^4\, N_e\, \frac{\mu_{\text{I}e}\mu_{\text{PT}}^2}{K_i K_f} \, |T_{fi}(\mathbf{q}_\perp,\mathbf{k},\alpha,\beta,\gamma)|^2. \tag{18}$$

If we work in terms of the rotational sudden approximation we can suppose the experiment with a large number of molecules whose orientations in space remain constant during the time of the collision and they are randomly distributed. Then, in order to obtain the 5DCS (7) we have to integrate Eq. (18) over the Euler angles (α,β,γ):

$$\frac{d^5\sigma}{d^2\mathbf{q}_\perp\, d^3\mathbf{k}} = \int d\alpha\, d\beta\, d\gamma\, \frac{d^8\sigma}{d^2\mathbf{q}_\perp\, d^3\mathbf{k}\, d\alpha\, d\beta\, d\gamma}. \tag{19}$$

For the energy range under consideration vibrational effects can be neglected, so we work in terms of the Frank Condon approximation, in which we suppose all the nuclei of the target molecule static at the equilibrium position with respect to the main molecular coordinates.

To calculate the transition amplitude T_{fi} (11), we employ a Nordsieck integral scheme together with a three-dimensional numerical integration as described in [33].

Working the expression of the transition amplitude (11) we can separate the part dependent on the Euler angles as a factor $D(\alpha,\beta,\gamma)$, which leads us to the following expression for the eight-differential transition amplitude [34,35].

$$T_{fi}(\mathbf{q}_\perp,\mathbf{k},\alpha,\beta,\gamma) = \sum_{lm}\sum_{\mu=-l}^{+l} S_{lm\mu}\, D_{lm\mu}(\alpha,\beta,\gamma), \tag{20}$$

where the sum over lm is extended over the values of expansion (6) through the Moccia basis set [27], and $S_{lm\mu}$ is given by

$$S_{lm\mu}(\mathbf{k},\mathbf{q}) = \frac{1}{(2\pi)^{9/2}} \int d^3\mathbf{p}\, s_{lm\mu}^{(1)}(\mathbf{p}) \left[s_{lm}^{(2)}(\mathbf{p}) + s_{lm}^{(3)}(\mathbf{p}) \right], \tag{21}$$

with

$$s_{lm\mu}^{(1)}(\mathbf{p}) = \frac{(4\pi)^2}{k} \sum_{l_1=0}^{\infty} \sum_{l_2=|l_1-l|}^{l_1+l} \sum_{m_1=-l_1}^{+l_1} (-i)^{l_1+l_2} A_{lm\mu,l_1 l_2 m_1}$$
$$\times \int_0^\infty r\, dr\, R_{lm}(r)\, u_{l_1}(k;r)\, e^{i\sigma_{l_1}}\, j_{l_2}(|\mathbf{p}+\mathbf{q}|r)$$
$$\times Y_{l_1,m_1}^*(\hat{\mathbf{k}})\, Y_{l_2,-m_1-\mu}(\widehat{\mathbf{p}+\mathbf{q}}), \tag{22}$$

$$s_{lm}^{(2)}(\mathbf{p}) = \int d^3\mathbf{r}_{e\rm P}\, e^{-i(\mathbf{p}-\mathbf{K}_f+\mathbf{K}_i)\cdot\mathbf{r}_{e\rm P}}\, e^{-z_c r_{e\rm P}}$$
$$\times\, _1F_1\left[i\frac{Z_{\rm P}}{k_{e\rm P}}, 1, i\, k_{e\rm P}\, r_{e\rm P} + i\, \mathbf{k}_{e\rm P}\cdot\mathbf{r}_{e\rm P} \right]$$
$$\times \int d^3\mathbf{R}_f\, e^{-i\,\mathbf{p}\cdot\mathbf{R}_f}\, e^{-z_c R_f}\, [-Z_{\rm P} V_{\text{mol}i}(\mathbf{R}_f)]$$
$$\times\, _1F_1\left[-i\frac{Z_{\rm P}\mu_{\rm PT}}{K_f}, 1, i\, K_f\, R_f + i\, \mathbf{K}_f\cdot\mathbf{R}_f \right], \tag{23}$$

$$s_{lm}^{(3)}(\mathbf{p}) = \int d^3\mathbf{r}_{e\rm P}\, e^{-i(\mathbf{p}-\mathbf{K}_f+\mathbf{K}_i)\cdot\mathbf{r}_{e\rm P}}\, e^{-z_c r_{e\rm P}} \left(-\frac{Z_{\rm P}}{r_{e\rm P}} \right)$$
$$\times\, _1F_1\left[i\frac{Z_{\rm P}}{k_{e\rm P}}, 1, i\, k_{e\rm P}\, r_{e\rm P} + i\, \mathbf{k}_{e\rm P}\cdot\mathbf{r}_{e\rm P} \right]$$
$$\times \int d^3\mathbf{R}_f\, e^{-i\,\mathbf{p}\cdot\mathbf{R}_f}\, e^{-z_c R_f}$$
$$\times\, _1F_1\left[i\frac{Z_{\rm P}\mu_{\rm PT}}{K_f}, 1, i\, K_f\, R_f + i\, \mathbf{K}_f\cdot\mathbf{R}_f \right]. \tag{24}$$

The angular part $A_{lm\mu,l_1 l_2 m_1}$ is a product of Clebsch-Gordan coefficients:

$$A_{lm\mu,l_1 l_2 m_1} = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}}\, \langle l_1\, l_2\, 0\, 0\,|\, l\, 0 \rangle$$
$$\times \langle l_1\, l_2, m_1, -m_1-\mu\,|\, l, -\mu \rangle, \tag{25}$$

$\mathbf{k}_{e\rm P}$ is the momentum of the ionized electron with respect to the projectile:

$$\mathbf{k}_{e\rm P} = \mathbf{k} - \frac{\mathbf{K}_f}{\mu_{\rm PT}}, \tag{26}$$

$R_{lm}(r)$ is the radial function (6), $u_{l_1}(k;r)$ is the radial part of the continuum wavefunction (16), $j_{l_2}(pr)$ the spherical Bessel functions, and z_c is a cutoff parameter, included to make convergent the Fourier transform of the continuum-continuum integrals involving the projectile and the ionized electron wavefunctions; in our case we have taken $z_c = 10^{-4}$ a.u.$^{-1}$. Smaller values of z_c do not lead to noticeable changes in the figures shown in this paper and only increase the computational times. Since we are concerned with large impact parameter collisions, the internuclear interaction potential present in (23) can be approximated by $V_{\text{mol}i}(R_f) = -\frac{1}{R_f}$.

The dependence in the orientation of the 8DCS given in Eq. (20) is included in the rotation matrix $D_{lm\mu}(\alpha,\beta,\gamma)$ defined by

$$D_{lm\mu}(\alpha,\beta,\gamma) = e^{-i\alpha\mu}\, d_{\mu m}^{(l)}(\beta)\, e^{-i\gamma m}, \tag{27}$$

where the functions $d^{(l)}_{\mu m}(\beta)$ are defined in [36,37] through the Jacobi polynomials. For a randomly oriented molecular target we can use the orthogonality relation,

$$\frac{1}{8\pi^2} \int_0^\pi \sin\beta\, d\beta \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma$$
$$\times D_{lm\mu}(\alpha,\beta,\gamma)\, D^*_{l'm'\mu'}(\alpha,\beta,\gamma) = \frac{1}{2l+1}\,\delta_{ll'}\,\delta_{mm'}\,\delta_{\mu\mu'},$$
$$(28)$$

and taking the square modulus of $T_{if}(\alpha,\beta,\gamma)$ it leads to a discrete sum over μ to determine the 5DCS:

$$\frac{d^5\sigma_{if}}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}} = \frac{1}{8\pi^2} \int_0^\pi \sin\beta\, d\beta \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma$$
$$\times \frac{d^8\sigma_{if}(\alpha,\beta,\gamma)}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}\, d\alpha\, d\beta\, d\gamma}$$
$$= \sum_{lm} \sum_{\mu=-l}^{+l} \frac{1}{2l+1}\, |S_{lm\mu}|^2. \qquad (29)$$

Finally, we have to sum the 5DCS corresponding to all the electrons of the target molecule. In practice, due to the increasing binding energies of the different orbitals, only the outer ones are relevant and will be considered as described in the following,

$$\frac{d^5\sigma}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}}(\boldsymbol{K}_f,\boldsymbol{k}) = \sum_i \frac{d^5\sigma_{if}}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}}. \qquad (30)$$

B. Born-C3 approximation

The Born-C3 approximation is a particular case of the Born-3DW model and consists of neglecting the low-r structure of the target potential $U_i(r)$ (15),

$$U_i^C(r) = -\frac{Z_T}{r}, \qquad (31)$$

where Z_T is the charge of the target after losing one electron. For an initially neutral target like methane, we then consider $Z_T = 1$.

In terms of the Born-C3 model, Eq. (17) is reduced to a radial Coulomb equation. Then the continuum wavefunction of the ionized electron $\chi^-(\boldsymbol{k};\boldsymbol{r})$ (16) is reduced to a Coulomb function $C^-(\boldsymbol{k};\boldsymbol{r})$ and in Eq. (22) one must replace the numerical partial waves $u_l(k;r)$ by the spherical Coulomb functions $F_l(k;r)$ and σ_l by σ_l^{Coul}.

The unoriented part of the transition amplitude $S_{lm\mu}$ (21) has then an analytical expression in terms of the Nordsieck integrals $Q_{nl\xi m\mu}(\boldsymbol{p},\boldsymbol{k})$ [38], with no need of doing the infinite sum (22).

$$\frac{(4\pi)^2}{k} \sum_{l_1=0}^\infty \sum_{l_2=|l_1-l|}^{l_1+l} \sum_{m_1=-l_1}^{+l_1} (-i)^{l_1+l_2}\, A_{lm\mu,l_1 l_2 m_1}$$
$$\times \int_0^\infty r\, dr\, \mathcal{R}_{nl\xi}(r)\, F_{l_1}(k;r)\, e^{i\sigma_{l_1}^{\text{Coul}}}\, j_{l_2}(|\boldsymbol{p}+\boldsymbol{q}|r)$$
$$\times Y^*_{l_1,m_1}(\hat{\boldsymbol{k}})\, Y_{l_2,-m_1-\mu}(\widehat{\boldsymbol{p}+\boldsymbol{q}}) = Q_{nl\xi m\mu}(\boldsymbol{p},\boldsymbol{k}). \qquad (32)$$

TABLE I. Coefficients of the expansion of the wavefunction of the orbital 2A$_1$ of CH$_4$.

l,m	0,0			3,2		
a,n,ξ	0.00877	1	9.500	$-0.100791\,i$	7	2.900
	-0.21248	1	5.500			
	0.98204	2	1.500	3,-2		
	0.05076	4	2.000	$0.100791\,i$	7	2.900
	-0.01799	4	3.000			

As R_{nl} is a linear combination of $\mathcal{R}_{nl\xi}$ through the Moccia coefficients, the integral (22) can be written as a simple linear combination of the Nordsieck ones.

III. CALCULATION

A. Radial wavefunctions of CH$_4$

The wavefunction of the molecular orbitals of CH$_4$ have been taken from the expansions of Moccia [27], for the five occupied orbitals of the CH$_4$ molecule. To calculate the total ionization cross section (30), we should extend the sum over all the five orbitals: 1A$_1$, 2A$_1$, 1T$_{2z}$, 1T$_{2x}$, and 1T$_{2y}$. As the inner orbital 1A$_1$ is tightly bound (-11.1949 a.u.), we can neglect the ionization coming from it and consider that only the outer ones 2A$_1$ and 1T contribute (-0.9024 and -0.5042 a.u., respectively). Due to the symmetry of the molecule, when the total 8DCS is averaged in space through (29), the three orbitals 1T will produce exactly the same result. So we calculate the total 5DCS (30) as

$$\frac{d^5\sigma}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}}(\boldsymbol{K}_f,\boldsymbol{k}) = \frac{d^5\sigma_{2\text{A}_1}}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}} + 3\,\frac{d^5\sigma_{1\text{T}_z}}{d^2\boldsymbol{q}_\perp\, d^3\boldsymbol{k}}. \qquad (33)$$

In the list of Moccia coefficients, we obtain the pairs (l,m) that contribute to the cross section for each molecular orbital (29) and the parameters for these radial expansions in Slater functions a,n,ξ (6). They are shown in Tables I and II (see [27]).

B. Partial waves

As the angular quantum number l of the continuum Schrödinger equation (17) is increased, the radial function $u_l(k;r)$ remains practically zero up to larger r values. This is easily seen by the relation between l and the classical impact parameter as usually taught in scattering theory courses. As

TABLE II. Coefficients of the expansion of the wavefunction of the orbital 1T$_{2z}$ of CH$_4$.

l,m	1,0			2,2		
a,n,ξ	1.25998	2	1.373	$-0.04731\,i$	4	2.400
	-0.05762	3	2.950	$0.23175\,i$	4	1.900
	-0.26738	4	2.950			
l,m	2,-2			3,0		
a,n,ξ	$0.04731\,i$	4	2.400	-0.08695	7	2.900
	$-0.23175\,i$	4	1.900			

a result, for l values larger than a certain l_{max}, the partial waves are not influenced by the internal structure of the molecular potential (i.e., the short interaction term), and the radial functions $u_l(k;r)$ tend to Coulomb functions as it is proposed by the Born-C3 model. We determinate l_{max} for each emission energy by studying how $u_l(k;r)$ converges to $F_l(k;r)$ as a function of l. In our case we have fixed the l_{max} value by asking $\delta_{l_{max}}$ to be lower than 10^{-4}. Once fixed this l_{max} value, we can calculate the integral (22) by correcting Nordsieck integrals as follows:

$$
\frac{(4\pi)^2}{k} \sum_{l_1=0}^{\infty} \sum_{l_2=|l_1-l|}^{l_1+l} \sum_{m_1=-l_1}^{+l_1} (-i)^{l_1+l_2} A_{lm\mu,l_1l_2m_1}
$$
$$
\times \int_0^{\infty} r\,dr\, R_{lm}(r)\, u_{l_1}(k;r)\, e^{i\sigma_{l_1}}\, j_{l_2}(|\boldsymbol{p}+\boldsymbol{q}|r)
$$
$$
\times Y_{l_1,m_1}^*(\hat{\boldsymbol{k}})\, Y_{l_2,-m_1-\mu}(\widehat{\boldsymbol{p}+\boldsymbol{q}})
$$
$$
= \frac{(4\pi)^2}{k} \sum_{l_1=0}^{\infty} \sum_{l_2=|l_1-l|}^{l_1+l} \sum_{m_1=-l_1}^{+l_1} (-i)^{l_1+l_2} A_{lm\mu,l_1l_2m_1}
$$
$$
\times \int_0^{\infty} r\,dr\, R_{lm}(r)\, F_{l_1}(k;r)\, e^{i\sigma_{l_1}^{Coul}}\, j_{l_2}(|\boldsymbol{p}+\boldsymbol{q}|r)
$$
$$
\times Y_{l_1,m_1}^*(\hat{\boldsymbol{k}})\, Y_{l_2,-m_1-\mu}(\widehat{\boldsymbol{p}+\boldsymbol{q}})
$$
$$
+ \frac{(4\pi)^2}{k} \sum_{l_1=0}^{l_{max}} \sum_{l_2=|l_1-l|}^{l_1+l} \sum_{m_1=-l_1}^{+l_1} (-i)^{l_1+l_2} A_{lm\mu,l_1l_2m_1}
$$
$$
\times \int_0^{\infty} r\,dr\, R_{lm}(r)\, j_{l_2}(|\boldsymbol{p}+\boldsymbol{q}|r)
$$
$$
\times [u_{l_1}(k;r)\, e^{i\sigma_{l_1}} - F_{l_1}(k;r)\, e^{i\sigma_{l_1}^{Coul}}]
$$
$$
\times Y_{l_1,m_1}^*(\hat{\boldsymbol{k}})\, Y_{l_2,-m_1-\mu}(\widehat{\boldsymbol{p}+\boldsymbol{q}})
$$
$$
= \frac{(4\pi)^2}{k} \sum_{l_1=0}^{\infty} \sum_{l_2=|l_1-l|}^{l_1+l} \sum_{m_1=-l_1}^{+l_1} (-i)^{l_1+l_2} A_{lm\mu,l_1l_2m_1}
$$

$$
\times \int_0^{\infty} r\,dr\, R_{lm}(r)\, e^{i\sigma_{l_1}^{Coul}}\, j_{l_2}(|\boldsymbol{p}+\boldsymbol{q}|r)
$$
$$
\times [u_{l_1}(k;r)\, e^{i\delta_{l_1}} - F_{l_1}(k;r)]
$$
$$
\times Y_{l_1,m_1}^*(\hat{\boldsymbol{k}})\, Y_{l_2,-m_1-\mu}(\widehat{\boldsymbol{p}+\boldsymbol{q}})
$$
$$
+ \sum_j Q_{n_jl_j\xi_jm\mu}(\boldsymbol{p},\boldsymbol{k}). \tag{34}
$$

With this method, we consider the infinite partial waves by adding, explicitly, a relatively small number of them. In other words, the essence of this method is to make use of the convenience of the Nordsieck integrals (which consider the infinite partial waves for the asymptotic Coulomb potential) and just correct the behavior of the first few partial waves for which the short interaction term of the molecular potential turns important. In Fig. 2 we consider an electron emitted with 5 eV and compare several partial waves for the molecular

(a)

(b)

FIG. 3. (Color online) Fully differential single ionization cross section for the collision $H^+ + CH_4$ versus the in-plane electron emission θ_e for an impact energy $E_0 = 2\,\text{MeV/amu}$ and an electron emission energy of $E_e = 5\,\text{eV}$. Three different momentum transfer q values are considered. Solid lines, Born-3DW model; dashed line, Born-3C model.
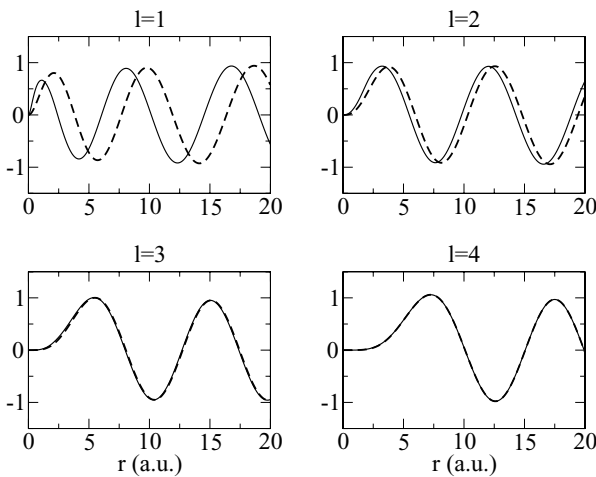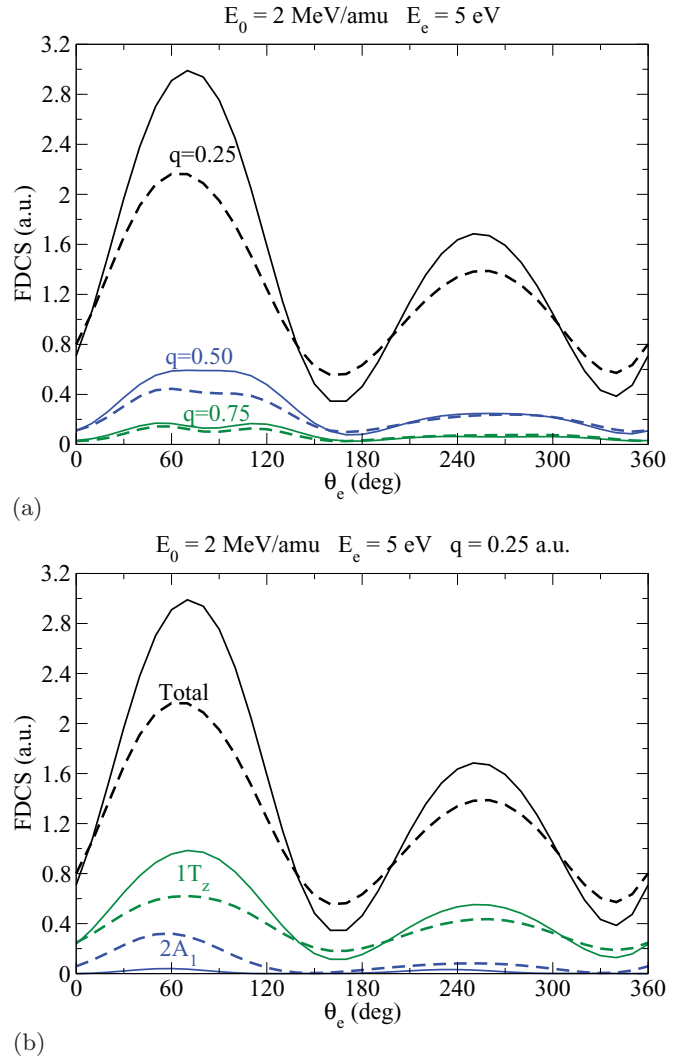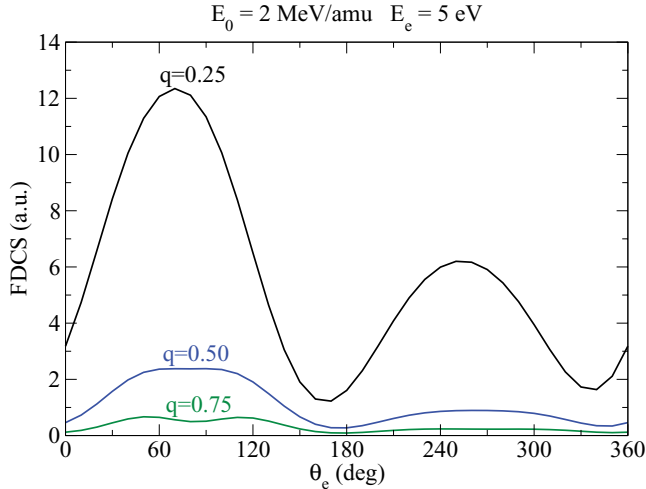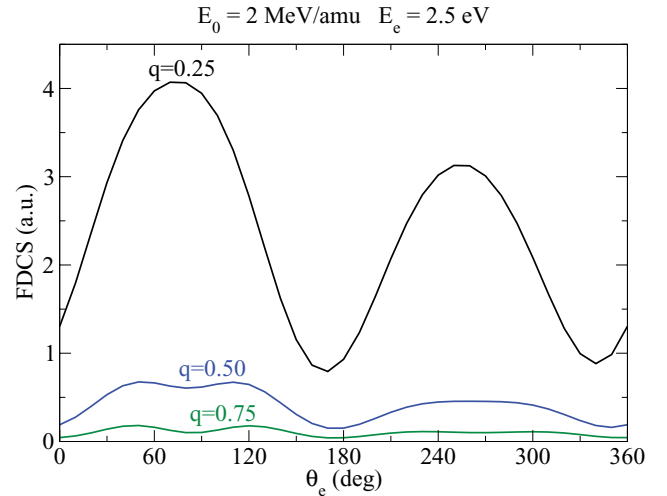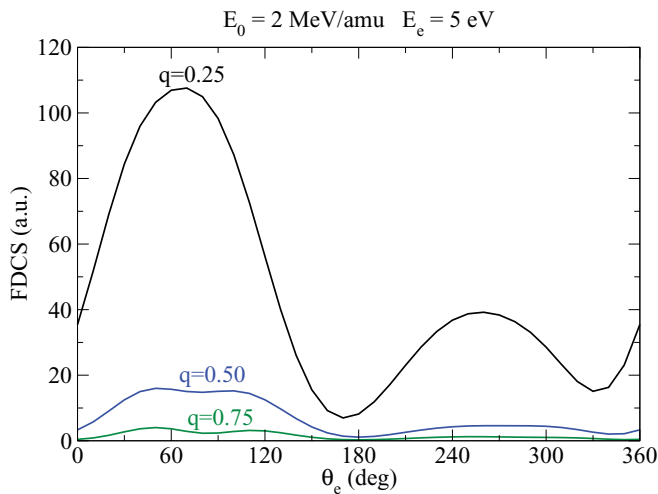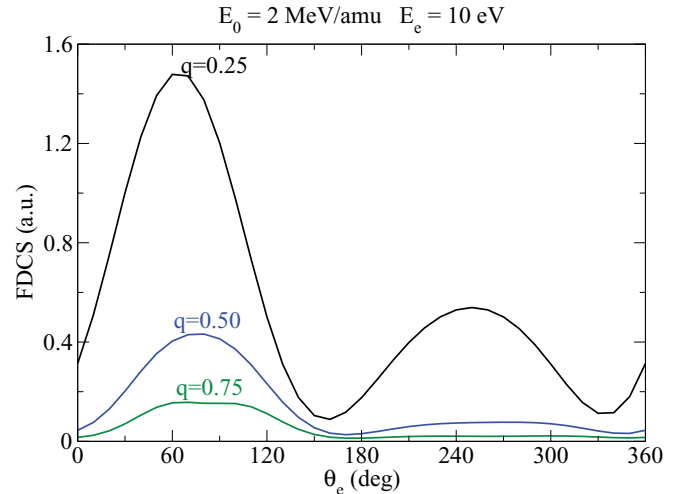
FIG. 2. Partial waves for several values of l for an energy of 5 eV. Solid lines, distorted wave (u_l) for CH₄ radially integrated potential (15); dashed lines, Coulomb waves (F_l) for the Coulomb potential $(-\frac{1}{r})$.

$E_0 = 2$ MeV/amu $E_e = 5$ eV

(a)

$E_0 = 2$ MeV/amu $E_e = 2.5$ eV

(a)

$E_0 = 2$ MeV/amu $E_e = 5$ eV

(b)

$E_0 = 2$ MeV/amu $E_e = 10$ eV

(b)

FIG. 4. (Color online) Single ionization FDCS for (a) He^{2+} + CH_4 and (b) C^{6+} + CH_4 collisions. Impact and emission energies as in Fig. 3.

FIG. 5. (Color online) Singly ionization FDCS for H^+ + CH_4 collisions. The impact energy is $E_0 = 2$ MeV/amu, and the emitted electron is ejected with energies: (a) $E_e = 2.5$ eV, (b) $E_e = 10$ eV.

potential $U_i(r)$ to those obtained for the Coulombic one $(-\frac{1}{r})$. We note that for $l_{max} = 4$ the radial function has already converged to the Coulombic one.

IV. RESULTS

We have calculated fully differential single ionization cross sections for collisions of H^+, He^{2+}, and C^{6+} on CH_4 initially in its electronic and vibrational ground state. The calculations have been done by an impact energy of 2 MeV/amu, and we have considered electron emission energies between 2.5 and 10 eV and transferred momentum values between 0.25 and 0.75 a.u. In all cases we consider the coplanar geometry in which the momenta of all the particles in the final channel live in the plane defined by $\mathbf{K}_i$ and $\mathbf{K}_f$. The angle θ_e is the emission angle of the electron in the collision plane measured clockwise from the beam direction. The projectiles are deflected counterclockwise.

In Fig. 3 we compare the FDCS obtained with the Born-3DW and the Born-C3 models. Due to the extension of the molecule, the internal structure of the potential is relevant, and

the results comparing both methods are expected to be quite different. However, a first glance at Fig. 3(a) would indicate that the two models here recalled lead to similar qualitative results: for low q values, the typical two-lobe structure is obtained consisting of the binary and recoil peaks. As the q value increases, the binary peak splits due to the p-state behavior of several of the Slater components of the 1T orbitals. The s nature of the $2A_1$ state partially helps to fill the gap region due to the splitting, leading to a wide structure as seen in Fig. 3(a). We note that the binary peak splitting for increasing q values has been recently studied in light particle impact single ionization of Ar [39]. A closer inspection [Fig. 3(b)] shows that our predictions with the Born-3DW model for the $2A_1$ state are much lower than those obtained with the Born-C3 model probably due to the larger ionization potential which indicates an electron bound closer to the nucleus as well as to the larger CH_4^+ charge seen by the emitted electron for r values lower than 2 a.u. These features are hard to infer from Fig. 3(a) due to the dominance of the 1T orbitals in the overall cross sections.

In Fig. 4 we show FDCS for 2 MeV/amu (a) He^{2+} and (b) C^{6+} collisions on CH$_4$. The emitted electron energy is 5 eV. The higher charge of the projectile not only leads to a larger cross section but is also seen to affect the binary to recoil ratio as expected.

In Fig. 5 we show FDCS for the 2 MeV/amu H$^+$ + CH$_4$ collision for electron emission energies of 2.5 and 10 eV. From this figure and Fig. 3, we observe how the binary to recoil peak ratio tends to increase as the electron emission energy increases.

V. CONCLUSIONS

In this work, we have developed a Born-3DW model in order to consider ion-molecule ionizing collisions at the fully differential level. The emitted electron-remaining core interaction has been represented by a non-Coulombic central potential which takes into account the variable charge seen by the electron as it leaves the reaction region. In particular, we have considered the CH$_4$ molecule for which Slater parametrizations for the different molecular orbitals have been available in the literature for a long time. The FDCS obtained with the Born-3DW model have been compared to those obtained by means of the much simpler Born-C3 method. We have concentrated on collision and emission energies that have been already explored with COLTRIMS (low q values, low-energy electron emission) for which we find that the results obtained with both models are in qualitative agreement. We note however that a more cautious inspection of this collision system (like isolation and exploration of the FDCS for the inner orbitals) would probably highlight the differences between both models and help gain insight into the underlying physics for future studies. Experimental data for this system would be highly desirable at this point.

This method can be easily extended to different target molecules, in particular H$_2$O, for which precise data is needed in biology and medicine.

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