

Electron impact experimental and theoretical fourfold differential cross section for CH₄

R El Mir^{1,2,3}, E M Staicu Casagrande^{3,4}, C Dal Cappello¹, A Naja², A Mansouri⁵ and I Kada⁵

¹ SRSMC, UMR CNRS 7565, Université de Lorraine, BP 70239, F-54506 Vandoeuvre-les Nancy, France

² LPM, EDST, Lebanese University, Tripoli, Lebanon

³ Université Paris-Sud, Institut des Sciences Moléculaires d'Orsay (ISMO), Bât. 351, F-91405 Orsay Cedex, France

⁴ CNRS, ISMO, Bat. 351, F-91405 Orsay Cedex, France

⁵ LPQSD, Département de Physique, Faculté des Sciences, Université de Setif1, 19000, Algeria

E-mail: elena-magdalena.staicu-casagrande@u-psud.fr

Abstract. New development of the 3C approximated model describing the fourfold differential cross section for double ionization of CH₄ will be reported. A corrective factor called Ward-Macek will take into account the repulsion between the two ejected electrons instead of the usual Gamow factor. To validate the developed model, we performed the coplanar (e, 3-1e) experiments for the double ionization of the methane target by electron impact at intermediate incident energy and different energy range for the pair of ejected electrons. Some agreement is found for the forward part of the angular distributions. The differences are discussed in terms of double ionization mechanisms.

1. Introduction

Collision has always been the main process leading to several discoveries in quantum world. The study of double ionization (DI) responds to the ever-increasing need for reliable cross-section data in diverse fields not only in physics but also in life sciences. DI by electron impact, called (e,3e) experiments see e.g. [1-6], is a main example of collision process during which all the electrons issued are determined in *triple coincidence* (or alternatively the residual ion plus two electrons [1,2]). Measuring the fully differential cross section for DI by performing kinematically complete experiments is a big challenge because of its small value. It is much easier to perform (e, 3-1e) experiments where only two of the three electrons in the final state are detected in *double coincidence* using the corresponding ionization potential IP^{2+} of the DI process.

Measurements of fourfold differential cross section (4DCS) for DI of rare gases such as He, Ne and Ar were reported in previous studies [1,7,8]. The corresponding results were obtained for coplanar geometry with equal and unequal energy sharing of ejected electron. Despite the difficulties imposed by the molecular nature, we published measurements of single ionization (SI) process of CH₄ [9] and compared the results to first order theoretical approaches. In addition, experiments of DI on methane have been performed with equal and unequal ejected electron energies ($E_b : E_c$) = (37 : 37) eV and ($E_b : E_c$) = (37 : 12) eV respectively [10]. Experimental results were compared to an approximation of the



well-known 3C model, labelled 2CWG, where the Gamow factor was used to describe the repulsion between the two ejected electrons. At the present time, only first order models are available because of the complexity nature of the molecular target.

The aim of the present work is to develop the theoretical approach used, leading to a better analysing of the molecular influence on the DI process. Note that the Gamow factor which is used generally in the 2CWG model, underestimates the 5DCS's amplitude especially when the two ejected electrons have the same ejected energy [11]. For this purpose we replaced it by a corrective one, obtaining the 2CWW model where the Ward-Macek factor is used instead of the Gamow factor. The second goal of this work is to validate our theoretical model, by comparing the theory with the (e, 3-1e) experimental data already published but also with new experiments with equal energy sharing of ejected electrons ($E_b : E_c$)=(12 : 12) eV.

2. Experiments

The experimental set-up used for the present experiments has been extensively described in [12] and it is identical to those used in [7,8]. Briefly, a monochromatic incident electron beam crosses the gas jet; the scattered electron is then detected in coincidence with the ejected electrons emitted in the collision plane defined by the incident and scattered momentum vectors, $\vec{k}_0$ and $\vec{k}_a$ respectively. This arrangement is known by 'coplanar geometry'. The electron-electron coincidence spectrometer is mainly characterized by three multi-angle toroidal analyzers coupled with positive sensitive detectors. Throughout this work, positive angles are counted clock wise starting from the incident electron beam direction. The 'fast' scattered electron, labelled 'a', is detected with a fixed energy $E_a=500$ eV at two symmetrical angles $\theta_a = + (6^\circ \pm 3^\circ)$ and $\theta_a = - (6^\circ \pm 3^\circ)$. Among the two ejected electrons resulting from the double ionization DI of the target (labelled 'b' for the faster and 'c' for the slower), we choose to detect only the faster with energy E_b in coincidence with the a-scattered electron, hence an (e, 3-1e) experiment. Of course, such distinction does not hold in the case of equal ejection energies, but we keep labelling 'b' the detected electron. The b-ejected electron is detected in almost the full angular range of the collision plane, i.e. $\theta_b = 20^\circ - 160^\circ$ and $\theta_c = 200^\circ - 340^\circ$ where 0° is defined by the incident beam direction. Although the emission direction of the third c-electron is unknown, its kinetic energy E_c is known from the energy conservation $E_0 - IP^{2+} = E_a + E_b + E_c$. The energy resolution of each analyser is set to 3 eV.

The experiments for CH_4 ($1t_2$) were performed with equal ejected electron energies ($E_b : E_c$) = (37 : 37) eV and (12 : 12) eV and unequal energies ($E_b : E_c$) = (37 : 12) eV. The experimental parameters are listed in table 1. The incident energy E_0 is consequently adjusted to fulfill the energy conservation requirement for the methane target under study, with a DI potential of the outermost orbital $1t_2$ IP^{2+} equal to 38eV. Here it is assumed that the DI process removing two electrons from the outermost orbital and leaving the ion in its ground state is dominant, but DI of the other orbital such as $2a_1$ cannot be excluded.

Table 1. Kinematical parameters for the DI process of CH_4 considered in this study. The last line indicates the forward and backward directions of ejection of the 'b'-electron (detected electron).

	$E_a = 500$ eV	$\theta_a = -6^\circ$	
E_0 (eV)	612	587	562
E_b (eV)	37	37	12
E_c (eV)	37	12	12
K (a.u)	0.93	0.83	0.75
θ_K / θ_{-K} (deg)	43/223	50/230	58/238

3. Theoretical framework

In the first Born approximation the six-fold differential cross section (6DCS) is given by

$$\sigma^6(\alpha; \beta; \gamma) = \frac{d^6\sigma(\alpha; \beta; \gamma)}{d\Omega_{Euler}d\Omega_a d\Omega_b d\Omega_c dE_b dE_c} = \frac{k_a k_b k_c}{k_0} |f_{B1}|^2 \quad (1)$$

for a molecular orientation defined by the Euler angles $(\alpha; \beta; \gamma)$ [12] where $d\Omega_{Euler} = \sin\beta d\beta d\alpha d\gamma$ and $d\Omega_a$, $d\Omega_b$ and $d\Omega_c$ denote the elements of solid angles for the scattered and the two ejected electrons b and c , respectively, whereas the energy intervals of the ejected electrons are represented by dE_b and dE_c . The momenta of the incident, the scattered, and the two ejected electrons are denoted by $\vec{k}_0$, $\vec{k}_a$, $\vec{k}_b$ and $\vec{k}_c$ respectively. In a $(e,3e)$ reaction the conservation of energy imposes: $\frac{k_0^2}{2} = \frac{k_a^2}{2} + \frac{k_b^2}{2} + \frac{k_c^2}{2} + IP^{2+}$. The first Born term f_{B1} is written as

$$f_{B1} = -\frac{1}{2\pi} \langle \exp(i\vec{k}_a \cdot \vec{r}_0) \Psi_f(\vec{k}_b, \vec{k}_c, \vec{r}_1 \dots \vec{r}_{10}) | V | \exp(i\vec{k}_0 \cdot \vec{r}_0) \Phi_i(\vec{r}_1 \dots \vec{r}_{10}) \rangle \quad (2)$$

where $\Phi_i(\vec{r}_1 \dots \vec{r}_{10})$ is the wave function of the initial state of the methane molecule and $\Psi_f(\vec{k}_b, \vec{k}_c, \vec{r}_1 \dots \vec{r}_{10})$ is the wave function for the double continuum state of the methane molecule. We here neglect the exchange effects between the incident particle and the ejected electrons because both the incident and the scattered electrons are faster than any ejected one. In equation (2), the potential V represents the Coulomb interaction between the incoming electron and the target and is written as

$$V = -\frac{6}{r_0} - \frac{1}{|\vec{r}_0 - \vec{R}_1|} - \frac{1}{|\vec{r}_0 - \vec{R}_2|} - \frac{1}{|\vec{r}_0 - \vec{R}_3|} - \frac{1}{|\vec{r}_0 - \vec{R}_4|} + \sum_{i=2}^{10} \frac{1}{r_{0i}} \quad (3)$$

where $R_1 = R_2 = R_3 = R_4 = R_{CH}$, $\vec{r}_i$ denotes the position vector of the i^{th} bound electron of the target with respect to the centre of the carbon nucleus, $\vec{r}_0$ the coordinate of the incident particle and $\vec{r}_{0i} = \vec{r}_0 - \vec{r}_i$.

The reduction of this 10-electron target problem to a two-electron target may be done by using the frozen-core approximation. In this case, the two target electrons are those which will be ejected during the double ionization. Then, the initial wave function describing the two active electrons is $|\Phi_i(\vec{r}_1, \vec{r}_2)\rangle$ and is given by the single centre wave function of Moccia [14]. In the present work, we are considering a DI process of the three orbitals ($1t_{2x}$, $1t_{2y}$ and $1t_{2z}$) of methane molecule (vapour gas). The 15 possible ion final states of CH_4^{++} have been considered. The final state wave function, which describes the two ejected electrons, is an approximate BBK wave function (called 2CWWM model) and it is given by:

$$\Psi_f(\vec{k}_b, \vec{r}_1, \vec{k}_c, \vec{r}_2) = \frac{1}{\sqrt{2}} [\Psi_c^-(\vec{k}_b, \vec{r}_1) \Psi_c^-(\vec{k}_c, \vec{r}_2) \pm \Psi_c^-(\vec{k}_b, \vec{r}_2) \Psi_c^-(\vec{k}_c, \vec{r}_1)] \times \varphi(|\vec{k}_b - \vec{k}_c|) \quad (4)$$

The sign $+$ corresponds to a wave function where the spin part is antisymmetric, while the sign $-$ refers to a symmetric spin part. Note that

$$\Psi_c^-(\vec{k}_b, \vec{r}_1) = \frac{1}{(2\pi)^{\frac{3}{2}}} \exp(i\vec{k}_b \cdot \vec{r}_1) \Gamma(1 - i\alpha) \exp\left(-\frac{\pi}{2}\alpha\right) {}_1F_1(i\alpha, 1, -i(\vec{k}_b \cdot \vec{r}_1 + k_b r_1)) \quad (5)$$

where $\alpha = -Z/k_e$ and $Z=2$ while the Ward-Macek factor [15] presented in Eq.(4), is

$$\varphi(|\vec{k}_b - \vec{k}_c|) = \exp\left(-\frac{\pi\chi_{bc}}{2}\right) \Gamma(1 - i\chi_{bc}) {}_1F_1(i\chi_{bc}, 1, -i|\vec{k}_b - \vec{k}_c|r_{12av})$$

with $\chi_{bc} = \frac{1}{|\vec{k}_b - \vec{k}_c|}$ and r_{12av} is an average of the distance $\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$.

The integration over the projectile coordinates (r_0) can be performed analytically. In order to make a comparison with $(e,3e)$ experiments we must average the above-described 6DCS over the Euler angles in order to obtain the total cross section for DI (5DCS), namely

$$\sigma^{(5)} = \frac{d^5\sigma}{d\Omega_a d\Omega_b d\Omega_c dE_a dE_b} = \frac{1}{8\pi^2} \iiint d\alpha d\gamma d\beta \sin\beta [\sigma^6(\alpha; \beta; \gamma)] \quad (6)$$

Knowing that DI proceeds by different pathway, it is common to consider that 5DCS is mainly dominated by three different mechanisms: shake-off, two-step 1 and two-step 2 known by SO, TS1 and

TS2 respectively. The two first-order mechanism SO and TS1 are included in the first Born approximation in a partial way [16]. The second-order process in the projectile-target interaction (TS2) can only be described by the second Born approximation B2 which needs a difficult eight numerical integration. Finally, four-fold differential cross section (4DCS) calculations defined as

$$\sigma^{(4)} = \iint \sigma^5 d\Omega_c = \frac{d^4\sigma}{d\Omega_a d\Omega_b dE_a dE_b} \quad (7)$$

were performed. It corresponds to the coincident detection of the scattered electron and only the ‘faster’ ejected electron.

4. Results and discussion

Experimental and theoretical results of fourfold differential cross section for DI (e, 3-1e) of the outermost $1t_2$ of CH_4 at $(E_b : E_c) = (37 : 37)$ and $(12 : 12)$ are shown in figures 1 (a)-(b) respectively and 4DCS of CH_4 at $(E_b : E_c) = (37 : 12)$ eV is shown in figure 2.

Relative experimental data have been normalized to the same absolute value of theory at the maximum of the forward lobe. Identically to the observation made in our previous work [9], we note some important common features: (i) the displaying of the angular distribution of the 4DCS of two-lobe structure: a forward lobe pointing roughly in the momentum transfer direction (θ_K) and a backward lobe pointing in the opposite direction (θ_{-K}), (ii) the breaking of symmetry about $\pm K$ and (iii) the exhibition of additional structures in these lobes.

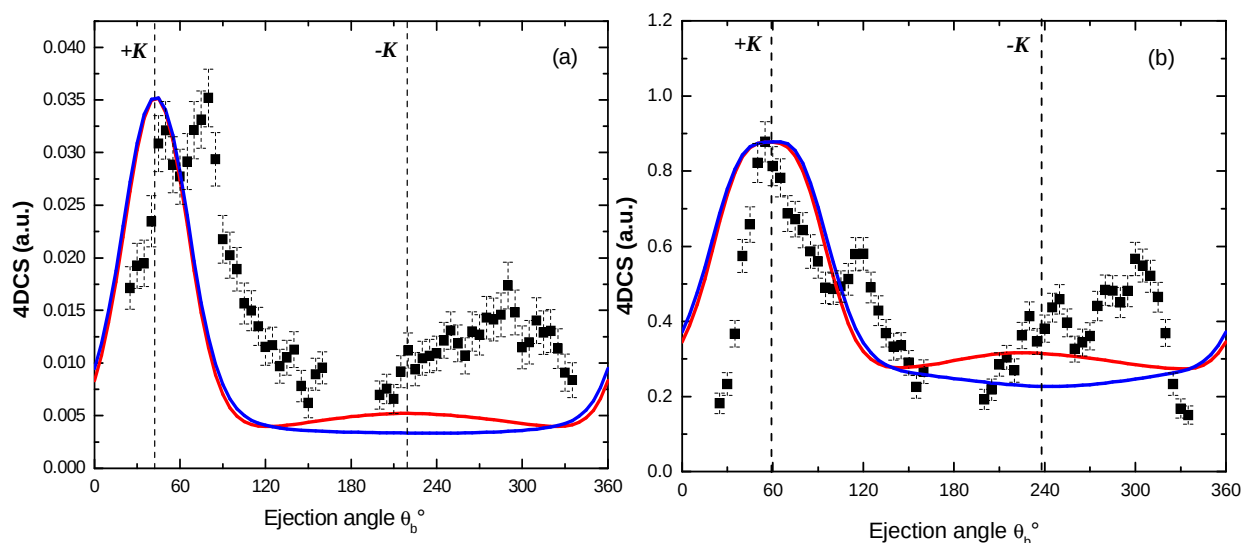


Figure 1. Four-fold differential cross sections (4DCS) for the double ionization of CH_4 . The scattered electron with energy $E_a = 500$ eV is detected at an angle $\theta_a = -6^\circ$ in coincidence with the fast-emitted electron with energy E_b , whereas the slow-emitted electron with energy E_c remains undetected. Panel (a): $(E_b : E_c) = (37 : 37)$ eV, (b): $(E_b : E_c) = (12 : 12)$ eV. Full squares are the experimental data, with one standard deviation statistical error bar. Blue and red solid curve present theoretical predictions from the first-order Born model using Ward-Macek factor and Gamow factor respectively. The absolute scale shown is that of 2CWWM to which the experiment is normalized for best visual fit at the maximum of the forward lobe. Results obtained by 2CWGM were multiplied by an arbitrary factor to fit the maximum of the forward lobe of 2CWWM. This factor is equal to 6.4 and 18.1 respectively for the cases $(E_b : E_c) = (37 : 37)$ eV and $(12 : 12)$ eV. The thin dashed lines indicate the direction of the momentum transfer (θ_K) and its opposite.

The two sets of the experimental data with equal energy sharing for the ejected electrons, $(E_b : E_c) = (37 : 37)$ eV and $(E_b : E_c) = (12 : 12)$ eV, show some differences in the intensity of the backward lobe

with respect to the forward one: when the energy of the outgoing electrons is lowered, the ratio between forward and backward lobe is decreasing. Another difference seems to be related to the width of the forward lobes: in the (12 : 12) case, the forward lobe is larger than in the (37 : 37) case. The post collision interactions which can explain this behavior are included in the theoretical model. We observed indeed that the theoretical results follow the same trend like the experimental results. However, in the comparison with the theoretical results important differences are found between this first-order theory and experiments:

- the existence of the backward structures which are not predicted by the B1 calculations;
- small additional structures in the forward lobe;
- in the (37 : 37) eV case an important shift with respect to the $\pm K$ directions of the two main lobes. In the (37 : 12) and (12 : 12) eV cases, this shift is less pronounced for the forward distribution, probably due to the fact that this lobe is much larger than in the (37 : 37) eV case and probably includes more contribution of the B1 mechanisms.

In the 4DCS of CH₄ at ($E_b : E_c$) = (37 : 12) eV important differences between the experiment and the theory are also presented. Experimental results show a second structure in the forward lobe and the backward lobe even if it is less important than in the other cases. This second structure is not reproduced by the theory and may be associated to the contribution of the high-order mechanisms.

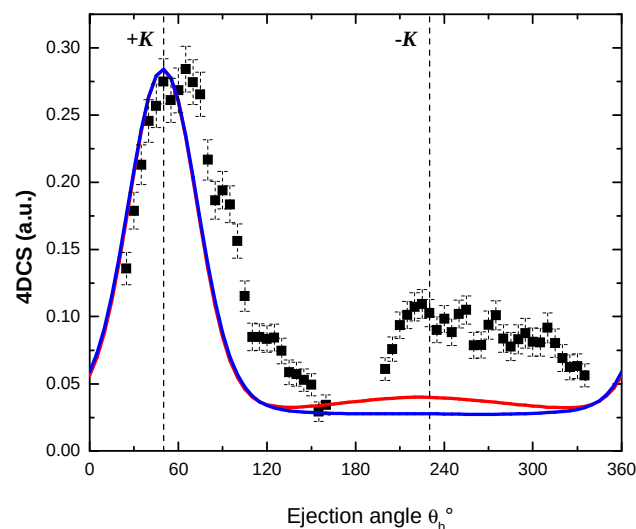


Figure2. Four-fold differential cross sections for (e, 3-1e) double ionization of CH₄ for unequal energy sharing ($E_b : E_c$) = (37 : 12) eV. Full squares are the experimental data, with one standard deviation statistical error bar. Blue and red solid curve present theoretical predictions from the first-order Born model using Ward-Macek factor and Gamow factor respectively. The absolute scale shown is that of 2CWWM to which the experiment is normalized for best visual fit at the maximum of the forward lobe. Results obtained by 2CWG were multiplied by an arbitrary factor to fit the maximum of the forward lobe of 2CWWM. In the present case, this factor is equal to 9.6. The thin dashed lines indicate the direction of the momentum transfer (θ_k) and its opposite.

To date, no theoretical second-order calculations for the present CH₄ (e, 3-1e) measurements are available.

5. Conclusion

In this paper we present the (e, 3-1e) studies for double ionization on methane. One of the motivations of this study is to present the last theoretical results obtained with a new way to describe the repulsion between the two ejected electrons. The experimental data have been compared with a B1 theoretical model which can reproduce the forward lobe of the angular distributions. The structures related to the

B1 mechanism are well described by the theory but additional structures appear in both forward and backward lobes. This suggests that other mechanisms are involved in the ionization and there are revealing limitations in the theoretical model which doesn't take into account the TS2 mechanism for instance.

References

- [1] Lahmam-Bennani A, Staicu Casagrande E M, Naja A, Dal Cappello C and Bolognesi P 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 105201
- [2] Lahmam-Bennani A, Dupre C and Duguet A 1989 *Phys. Rev. Lett.* **63** 1582
- [3] Dupre C, Lahmam-Bennani A and Duguet A 1991 *Meas. Sci. Technol.* **2** 327
- [4] Taouil I, Lahmam-Bennani A, Duguet A and Avaldi L 1998 *Phys. Rev. Lett.* **81** 4600
- [5] Jia C C, Lahmam-Bennani A, Duguet A, Lecas M and Dal Cappello C 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 110313
- [6] Naja A, Staicu Casagrande E M, Ren X G, Catoire F, Lahmam-Bennani A, Dal Cappello C and Whelan C T 2007 *J. of Phys. B: At. Mol. Opt. Phys.* **40**, 2871-84
- [7] Staicu Casagrande E M, Li C, Lahmam-Bennani A, Dal Cappello C, Schultz M and Ciappina M 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 055201
- [8] Li C, Lahmam-Bennani A, Staicu Casagrande E M and Dal Cappello C 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 115201
- [9] Nixon K L, Murray A J, Chaluvadi H, Amami S, Madison D H and Ning C 2012 *J. Chem. Phys.* **136** 094302
- [10] Staicu Casagrande E M, Li C, Lahmam-Bennani A and Dal Cappello C 2014 *J. Phys. B: At. Mol. Opt. Phys.* **47** 115203
- [11] Dal Cappello C and Ancarani L U 2008 *J. Phys. B: At. Mol. Opt. Phys.* **41** 208001
- [12] Catoire F, Staicu Casagrande E M, Lahmam-Bennani A, Duguet A, Naja A, Ren X G, Lohmann B and Avaldi L 2007 *Rev. Sci. Instrum.* **78** 013108
- [13] Kada I, Mansouri A, Dal Cappello C, Hervieux P A and Roy A C 2009 *J. Phys. B: At. Mol. Opt. Phys.* **42** 025201
- [14] Moccia R 1964 *J. Chem. Phys. A.* **40** 2186
- [15] Ward S J and Macek J H 1994 *Phys. Rev. A* **49** 1049
- [16] Popov Yu V, Dal Cappello C, Joulakian B and Kuzmina N M 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 1599