Ab initio calculation of differential and total cross sections for the ionization of water vapor by protons

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(Received 6 August 2006; published 28 February 2007)

We present both differential and total cross sections for the direct ionization of water vapor by protons in the incident energy range 0.1–100 MeV. Different theoretical models are investigated within the framework of the Born approximation in order to evaluate the influence of each pairwise Coulomb interaction term among the ejected electron, the scattered proton, and the residual ionized target in the final state. In all these models, the ground state of the water molecule is described by means of an accurate molecular wave function proposed by Moccia [J. Chem. Phys. **40**, 2186 (1964)]. The results of these full *ab initio* quantum-mechanical treatments are compared to experimental data. Good agreement is generally observed, showing that sophisticated Born models are sufficient to explain all the experimental data, including doubly differential, singly differential, and total cross sections.

DOI: 10.1103/PhysRevA.75.022720 PACS number(s): 34.80.Dp

I. INTRODUCTION

It has been well known for a long time that ionization of atoms and molecules by fast charged particles (ions) is of prime importance in a large number of areas, including plasma physics, radiation physics, and in the study of penetration of charged particles through matter [1–3]. Recently, it has also been shown that experimental and theoretical data about the ionization of biological systems were needed in fundamental studies of charged particle interaction in biological material (and more precisely in heavy-ion cancer therapy [4]), which is commonly modeled by water. Under these conditions, it appears crucial to possess accurate differential and total ionization cross sections for light and heavy ions.

In fact, experimental measurements of ionization cross sections of water vapor by light and heavy charged particles are extremely scarce. The first extensive work was given by Toburen and Wilson [5], who measured doubly differential cross sections (DDCS) for 300–1500 keV protons, and more recently Toburen *et al.* [6] reported DDCS for 300–2000 keV He^+ and He^{2+} ions. Later on, Rudd *et al.* [7,8] performed experiments on the ionization of water vapor by 7–4000 keV proton and 5–450 keV He^+ ion impact and reported total direct cross sections (without capture). More recently, Bolorizadeh and Rudd [9] have extended the previous work of Rudd *et al.* [7] to the DDCS measurements for the ejection of electrons during the ionization process of water vapor by 15–150 keV proton impact. Finally, the multiple ionization and the fragmentation of water have been studied by Werner *et al.* [10] for fast protons and He^+ ions by using a position- and time-sensitive multiparticle detector: good agreement was also observed with the previous measurements of Rudd *et al.* [7] for the total cross sections (TCS). Furthermore, Gobet *et al.* [11] have determined a complete set of cross sections for the ionization of a water molecule by proton impact in the energy range 20–150 keV including the total and partial cross sections for H^+ and H_2O^+ fragment production. They also found TCS in good agreement with the measurements of Rudd *et al.* [7] and those of Werner *et al.* [10]. Recently, Gobet *et al.* [12] presented a full set of absolute partial cross sections corresponding to H^+, H_2O^+, OH^+, O^+, and O^{2+}, which allows a detailed comparison between their cross sections for direct ionization of water by proton impact and the electron impact ionization data of Straub *et al.* [13]. Very recently, Oshawa *et al.* [14] have reported absolute doubly differential cross sections for the angular distributions of secondary electrons produced in collisions of 6.0 and 10.0 MeV/u He^{2+} ions with water vapor and have evaluated the singly differential cross sections (SDCS) by integrating their DDCS data.

Theoretically, few models have been proposed to study the direct ionization of water by proton impact. Senger *et al.* [15,16] have applied the plane-wave Born approximation (PWBA) using different molecular orbitals, modifying the form factors and making corrections for binding energies of inner shells. As a matter of fact, Senger *et al.* started from the well-known formula of Kuyatt and Jorgensen [17] for the ionization of atomic hydrogen by proton impact and its extension to the other *L* and *M* subshells by Khandelwal and Merzbacher [18,19] and Choi *et al.* [20]. In addition, they applied the Salin factor [21] to account for the mechanism of electron transfer to the continuum. Recently, Olivera *et al.* [22] have used the continuum-distorted-wave–eikonal-initial-state (CDW-EIS) approximation (Fainstein *et al.* [23]), which represents the first order of a distorted-wave series by including the distortions due to the long-range Coulomb potential in both the initial and final channels. The latter were also introduced as multiplicative factors to the initial bound and final continuum states of the molecular target. It was then possible to take into account the two-center effects that were not present in the PWBA. Unfortunately, Olivera *et al.* [22] (like Senger *et al.* [15,16]) never used an accurate wave function to describe the molecular states since they represented the orbitals of the water molecule by the complete neglected differential overlap (CNDO) model (Siegbahn *et al.* [24]), in which the molecular orbitals were expressed by linear combinations of atomic orbitals of the constituents.

In the present work, we describe the theoretical approach we have adopted to treat the ionization process of the water molecule by proton impact. Three different models have been investigated, all of them describing the ground state of the target molecule by means of *an accurate molecular wave function* developed in terms of Slater-type-orbital functions, all centered at a common origin, namely upon the heaviest nucleus, i.e., the oxygen atom. They refer to the equilibrium configurations calculated in the self-consistent-field (SCF) method and agree very well with some of the experimental data like the electric dipole moment, the ionization potential, the binding length O-H, the equilibrium distance H-H, and the molecular angle H-O-H (for more details, see [25]). Among the three different models, which differ from each other in the choice of the final-state wave function, (i) the first one consists in introducing the ejected electron-residual target interaction as in the PWBA, (ii) the second one has the scattered proton-ionized target interaction added (called the 2CW model), and finally (iii) the third one (called the BBK model since it was introduced by Brauner *et al.* [26])) takes into account the pairwise interactions of the ionized target with the projectile and the ejected electron, and the attraction between the ejected electron and the scattered proton. Three Coulomb waves are then used in this BBK model to take into account these three interactions.

Section II deals with the different theoretical models we have developed in the present work by highlighting their discrepancies and similarities. In Sec. III, the DDCS (calculated in each model), the SDCS, and the TCS are compared to a large set of experimental data. Finally, a conclusion about the modeling of the water molecule ionization by proton impact is given.

Atomic units are used throughout unless otherwise indicated.

II. THEORY

The direct ionization of the water molecule by a proton can be schematized by

$$p + H_2O \rightarrow p + H_2O^+ + e^-. \tag{1}$$

We consider that a fast proton of charge z_p ($z_p=1$ here), mass μ, and initial momentum $\vec{k}_i$ ionizes a stationary water molecule. The final state of the system is then characterized by a scattered proton of momentum $\vec{k}_s$ and an ejected electron of momentum $\vec{k}_e$. The fourfold differential cross section for this process, i.e., differential in the energy of the ejected electron $k_e^2/2$, differential in the direction of the ejected electron $d\Omega_e$, differential in the energy of the scattered proton $k_s^2/2\mu$, and differential in the direction of the scattered particle $d\Omega_s$, is given by (Massey and Mohr [27])

$$\frac{d^4\sigma}{k_s^2 dk_s d\Omega_s k_e^2 dk_e d\Omega_e} = \frac{\mu}{k_i}|T_{fi}|^2 \delta\left(\frac{k_i^2}{2\mu} - |I_i| - \frac{k_s^2}{2\mu} - \frac{k_e^2}{2} - \frac{(\vec{K}-\vec{k}_e)^2}{2M_{ion}}\right), \tag{2}$$

where I_i is the ionization energy (i.e., the binding energy of the molecular subshell ionized) and M_{ion} is the mass of the residual water ion. In Eq. (2), $\vec{K}=\vec{k}_i-\vec{k}_s$ is the transferred momentum from the incident proton to the water target.

In the experiments considered here, the energy and the solid angle of the scattered proton are not measured and the doubly differential cross section (DDCS) is given by

$$\frac{d^2\sigma}{d\Omega_e dE_e} = \frac{\mu k_e}{k_i}\int |T_{fi}|^2 \delta\left(\frac{k_i^2}{2\mu} - |I_i| - \frac{k_s^2}{2\mu} - \frac{k_e^2}{2} - \frac{(\vec{K}-\vec{k}_e)^2}{2M_{ion}}\right) d\vec{k}_s. \tag{3}$$

The scattering amplitude is given by

$$T_{fi} = \frac{-z_p}{2\pi}\langle \psi_f | V | \psi_i \rangle. \tag{4}$$

where V represents the interaction between the incoming proton and the target and is written as

$$V = -\frac{8}{r_0} - \frac{1}{|\vec{r}_0 - \vec{R}_1|} - \frac{1}{|\vec{r}_0 - \vec{R}_2|} + \sum_{i=1}^{i=10} \frac{1}{|\vec{r}_0 - \vec{r}_i|}, \tag{5}$$

where $R_1=R_2=R_{\text{OH}}$ represents the binding length O-H ($R_{\text{OH}}=1.81$ a.u. [25]) and $\vec{r}_i$ is the position of the ith bound electron of the target with respect to the oxygen nucleus and $\vec{r}_0$ that of the passing proton with respect to the oxygen nucleus.

The initial state of the system $\{p-H_2O\}$ is then described by the product of a plane wave $\phi(\vec{k}_i,\vec{r}_0)$, which represents the incident proton and the ground-state wave function of the water molecule,

$$|\psi_i\rangle = |\phi(\vec{k}_i,\vec{r}_0)\varphi_i(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_{10})\rangle. \tag{6}$$

The ten bound electrons are distributed among the five one-center molecular wave functions $\nu_j(\vec{r})$ (with j ranging from 1 to 5) corresponding to the five molecular orbitals $^1B_1$, $^3A_1$, $^1B_2$, $^2A_1$, and $^1A_1$, respectively. Each of them is expressed by linear combinations of Slater-type functions [25] and is written as

$$\nu_j(\vec{r}) = \sum_{k=1}^{N_j} a_{jk} \Phi^{\xi_{jk}}_{n_{jk}l_{jk}m_{jk}}(\vec{r}), \tag{7}$$

where N_j is the number of Slater functions used in the development of the jth molecular orbital and a_{jk} is the weight of each real atomic component $\Phi^{\xi_{jk}}_{n_{jk}l_{jk}m_{jk}}(\vec{r})$.

In Eq. (7), $\Phi^{\xi_{jk}}_{n_{jk}l_{jk}m_{jk}}(\vec{r})$ is written as

$$\Phi^{\xi_{jk}}_{n_{jk}l_{jk}m_{jk}}(\vec{r}) = R^{\xi_{jk}}_{n_{jk}}(r) S_{l_{jk}m_{jk}}(\hat{r}), \tag{8}$$

where the radial part $R^{\xi_{jk}}_{n_{jk}}(r)$ is given by

$$R^{\xi_{jk}}_{n_{jk}}(r) = \frac{(2\xi_{jk})^{n_{jk}+1/2}}{\sqrt{(2n_{jk})!}} r^{n_{jk}-1} e^{-\xi_{jk}r}, \tag{9}$$

and where $S_{l_{jk}m_{jk}}(\hat{r})$ is the so-called real solid harmonic [28] expressed by

$$S_{l_{jk}m_{jk}}(\hat{r}) = \left(\frac{m_{jk}}{2|m_{jk}|}\right)^{1/2}\left\{ Y_{l_{jk}-|m_{jk}|}(\hat{r}) + (-1)^{m_{jk}}\left(\frac{m_{jk}}{|m_{jk}|}\right) Y_{l_{jk}|m_{jk}|}(\hat{r})\right\} \quad \text{if } m_{jk} \neq 0,$$

$$S_{l_{jk}0}(\hat{r}) = Y_{l_{jk}0}(\hat{r}) \quad \text{if } m_{jk} = 0. \tag{10}$$

Let us note that the molecular energy and the electric dipole moment computed by using this wave function are very close to the experimental values. Moreover, Champion *et al.* [29] have obtained a good agreement between the electron momentum spectroscopy (EMS) data of Bawagan *et al.* [30] and the theoretical triply differential cross sections (TDCS) using the wave functions of Moccia [25].

The final state is characterized by the product of two wave functions as

$$|\psi_f\rangle = |\psi_{f1}\psi_{f2}\rangle. \tag{11}$$

where ψ_{f1} describes the system constituted by an ejected electron and a scattered proton while ψ_{f2} describes the nine bound electrons of the target. The so-called frozen-core approximation supposes that the ion is described by the same single-particle basis (7)–(10) as the water molecule. This model allows reducing the molecular problem with ten electrons to the two-body problem with only one active electron. Such a simplification leads to the scattering amplitude given by

$$T_{f1} = \frac{-z_p}{2\pi}\left\langle \psi_f(\vec{k}_s,\vec{r}_0,\vec{k}_e,\vec{r}_1)\left|\frac{1}{r_{01}} - \frac{1}{r_0}\right|\phi(\vec{k}_i,\vec{r}_0)\nu_j(\vec{r}_1)\right\rangle. \tag{12}$$

It is important to note that these wave functions $\nu_j(\vec{r}_1)$ correspond to a particular orientation of the molecular target given by the Euler angles (α,β,γ) (see [31,32] for more details). Thus, the differential cross sections we have calculated correspond in fact to the ionization of an oriented water molecule. Under these conditions, we have to average these differential cross sections over the Euler solid angle to obtain differential cross sections comparable to those experimentally measured. The Euler integration is analytically carried out thanks to the property of the rotation matrix [31,32], whereas the remaining integration over $d\Omega_s$ is numerically performed. Finally, let us note that this procedure is performed for each of the five orbitals of the water molecule, and the differential cross sections presented here correspond to "global" differential cross sections obtained by summing up all the subshell contributions weighted by the number N_{elec} of electrons per orbital, i.e., $N_{\text{elec}}=2$.

We now consider below few models for describing the final state (the scattered proton and the ejected electron).

(i) In the first model [we call it distorted plane wave Born approximation (DPWBA)], the scattered proton is described by a plane wave, whereas the ejected electron is described by a distorted wave,

$$\psi_{f1}(\vec{k}_s,\vec{r}_0,\vec{k}_e,\vec{r}_1) = \exp(i\vec{k}_s\cdot\vec{r}_0)\varphi_c(\vec{k}_e,\vec{r}_1), \tag{13}$$

with

$$\varphi_c(\vec{k}_e,\vec{r}) = \sum_{l=0}^{\infty}\sum_{m=-l}^{m=+l}(i)^l\exp[-i(\sigma_l+\delta_l)] \times\frac{F_l(k_e;r)}{k_e r}Y^*_{lm}(\hat{k}_e)Y_{lm}(\hat{r})\sqrt{\frac{2}{\pi}}, \tag{14}$$

where σ_l and δ_l represent the Coulomb phase shift and the short-range phase shift associated with the distortion potential $W(r)$, respectively. The radial regular function $F_l(k_e;r)$ is the solution of the differential equation

$$\left[\frac{1}{2}\frac{d^2}{dr^2} + E_e - \frac{l(l+1)}{2r^2} - W(r)\right]F_l(k_e;r) = 0, \tag{15}$$

and has an asymptotic behavior given by

$$F_l(k_e;r) \approx \sin\left(k_e r - l\frac{\pi}{2} + \frac{1}{k_e}\ln(2k_e r) + \sigma_l + \delta_l\right). \tag{16}$$

Let use note that when $\delta_l=0$, the function $\varphi_c(\vec{k}_e,\vec{r})$ becomes a Coulomb wave, which can be rewritten as

$$\varphi_c(\vec{k}_e,\vec{r}) = \frac{\exp(i\vec{k}_e\cdot\vec{r})}{(2\pi)^{3/2}}{}_1F_1(-iz_e/k_e,-i(\vec{k}_e\cdot\vec{r}+k_e r)) \times\exp\left(\frac{\pi z_e}{2k_e}\right)\Gamma(1+iz_e/k_e). \tag{17}$$

In this model, denoted henceforth as the FBA-CW model, z_e corresponds to the effective ionic charge and will be taken to be equal to 1 (Brothers and Bonham [33]).

(ii) In a second model, the scattered proton and the ejected electron are both described by Coulomb waves (2CW) (Schulz [34]). This leads to a final state described by

$$\begin{aligned}\psi_{f1}(\vec{k}_s,\vec{r}_0,\vec{k}_e,\vec{r}_1) &= \frac{\exp(i\vec{k}_s\cdot\vec{r}_0)}{(2\pi)^{3/2}}{}_1F_1(i\mu z_s/k_s,1,-i(\vec{k}_s\cdot\vec{r}_0+k_s r_0)) \\ &\times\exp\left(\frac{-\pi z_s\mu}{2k_s}\right)\Gamma(1-iz_s\mu/k_s) \\ &\times\frac{\exp(i\vec{k}_e\cdot\vec{r}_1)}{(2\pi)^{3/2}}{}_1F_1(iz_e/k_e,1,-i(\vec{k}_e\cdot\vec{r}_1+k_e r_1)) \\ &\times\exp\left(\frac{\pi z_e}{2k_e}\right)\Gamma(1+iz_e/k_e),\end{aligned} \tag{18}$$

where the charges seen by the scattered proton and the ejected electron are defined as the effective ionic charges with $z_e=z_s=1$.

(iii) In a third approach, we have used one of the most sophisticated models, called the BBK model, which describes the final state by

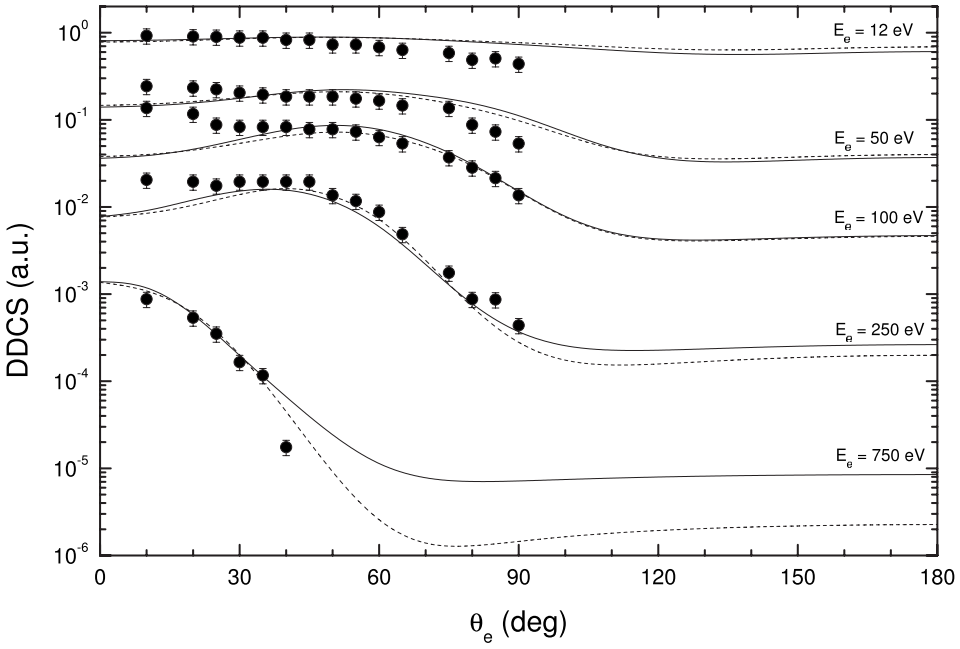

FIG. 1. Doubly differential cross sections for single ionization of water vapor by 0.3 MeV protons for different electron energies as a function of the electron angle. Theory: solid line, FBA-CW model; dashed line, DPWBA model. Experiments: black circles, from Toburen and Wilson [5].

$$\psi_{f1}(\vec{k}_s,\vec{r}_0,\vec{k}_e,\vec{r}_1) = \frac{\exp(i\vec{k}_s\cdot\vec{r}_0)}{(2\pi)^{3/2}}{}_1F_1(i\mu z_s/k_s,1,-i(\vec{k}_s\cdot\vec{r}_0+k_sr_0))$$
$$\times\exp\left(\frac{-\pi z_s\mu}{2k_s}\right)\Gamma(1-iz_s\mu/k_s)\frac{\exp(i\vec{k}_e\cdot\vec{r}_1)}{(2\pi)^{3/2}}{}_1F_1(iz_e/k_e,1,-i(\vec{k}_e\cdot\vec{r}_1+k_er_1))$$
$$\times\exp\left(\frac{\pi z_e}{2k_e}\right)\Gamma(1+iz_e/k_e){}_1F_1\left(-i\mu/|\vec{k}_s-\mu\vec{k}_e|,1,-i\left\{\frac{(\vec{k}_s-\mu\vec{k}_e)}{\mu+1}\cdot(\vec{r}_0-\vec{r}_1)+\left|\frac{(\vec{k}_s-\mu\vec{k}_e)}{\mu+1}\right|r_{01}\right\}\right)$$
$$\times\exp\left(\frac{\pi\mu}{2|\vec{k}_s-\mu\vec{k}_e|}\right)\Gamma(1+i\mu/|\vec{k}_s-\mu\vec{k}_e|), \tag{19}$$

where the charges seen by the scattered proton and the ejected electron are also defined as the effective charges with $z_e=z_s=1$. For this model, we have the well-known asymptotically correct Coulomb three-body wave function for the ejected electron and the scattered proton in the field of the residual ion.

Finally, we notice that the amplitude T_{fi} decreases fast when the momentum transfer K increases. Only small values of K contribute to the integration over $d\vec{k}_s$ in Eq. (3). Then we can neglect the term $(\vec{K}-\vec{k}_e)^2/2M_{\text{ion}}$ in the δ function of Eq. (3) and get

$$\frac{d^2\sigma}{d\Omega_e dE_e} = \frac{\mu k_e}{k_i}\int |T_{fi}|^2\delta\left(\frac{k_i^2}{2\mu}-|I_i|-\frac{k_s^2}{2\mu}-\frac{k_e^2}{2}\right)d\vec{k}_s, \tag{20}$$

III. RESULTS AND DISCUSSION

One aim of this work is to find a theoretical model able to describe most of the available experimental data concerning doubly differential, singly differential, and total cross sections for the water ionization process.

A. DDCS calculations

Up to now, there have only been two sets of experimental data about the ionization of water vapor by proton impact, namely those of Toburen and Wilson [5] and those more recently performed by Bolorizadeh and Rudd [9]. These data are absolute and correspond to proton energies of 1.5, 1, 0.5, and 0.3 MeV (Toburen and Wilson [5]) and to 15, 100, and 150 keV (Bolorizadeh and Rudd [9]).

Figures 1, 2, 3, and 4 show a comparison between the experimental DDCS data [5] and the results of two theoretical models (FBA-CW and DPWBA) at incident energies of 0.3, 0.5, 1.0, and 1.5 MeV, respectively. We generally observe good agreement between the FBA-CW model and the data for all electron energies (from 12 to 2200 eV) except for small angles at some fixed energies of the ejected electron (100, 250, and 750 eV). This can be explained by the fact that the process of charge transfer to the continuum (ECC),

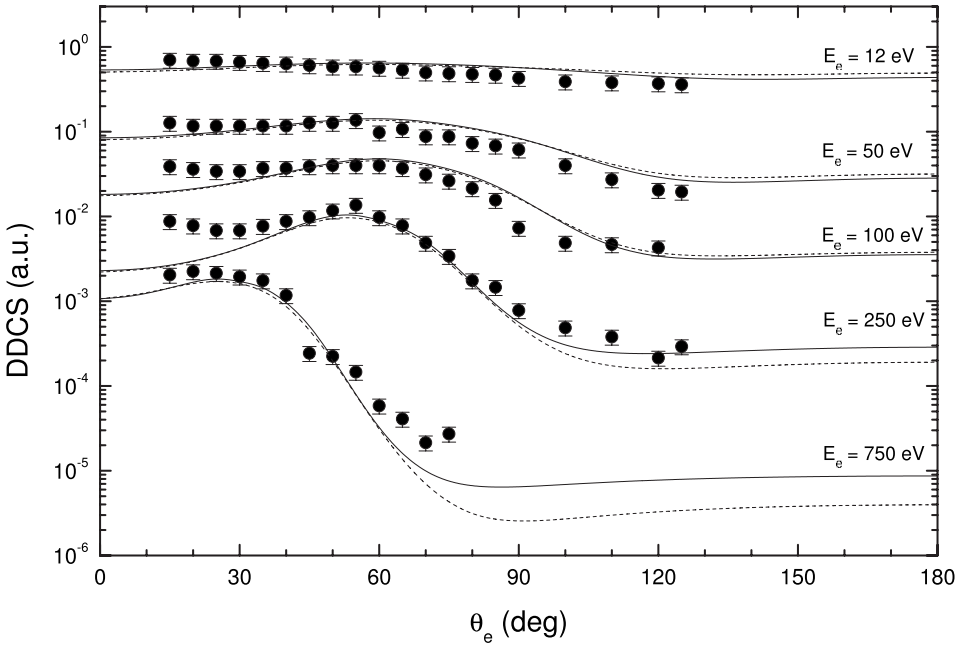

FIG. 2. Same as in Fig. 1 for 0.5 MeV proton impact.

which causes an increase of the differential cross sections, is not included in our first models. This process is conspicuous when the velocity of the ejected electron is close to those of the scattered proton. This means that an electron is "captured" from the target molecule into a continuum state of the proton and then emitted in the moving frame of the proton. This effect can also be called the Thomas effect [35] and corresponds to a classical capture. Furthermore, we see that the DPWBA and FBA-CW methods yield nearly identical cross sections. They, however, begin to differ from each other by a small amount, especially with increasing angles and energies of the ejected electron at fixed incident energy. In fact, the present calculations show that the effect of the short-range phase shift associated with the distortion potential is not very significant in the present region of experimental study.

Figure 5 shows a typical plot of DDCS as a function of ejected electron angle for a fixed ejection energy of 250 eV at the incident energy of 1.5 MeV. We see that all the FBA-CW contributions of each orbital are significant and needed to estimate the DDCS. Although the contribution of the $^1A_1$ is generally weak, we notice its importance for large values of the ejected angle.

Figure 6 is a detailed comparison between the DDCS calculated in each of the theoretical models previously described and the experimental measurements for an incident proton energy of 0.5 MeV and an ejected electron of 250 eV [5]. This case corresponds to a big rise of the DDCS for small angles due to the process of charge transfer to the continuum. We clearly observe that both the FBA-CW and 2CW models are unable to explain the large enhancement of the DDCS for small angles because none of these models

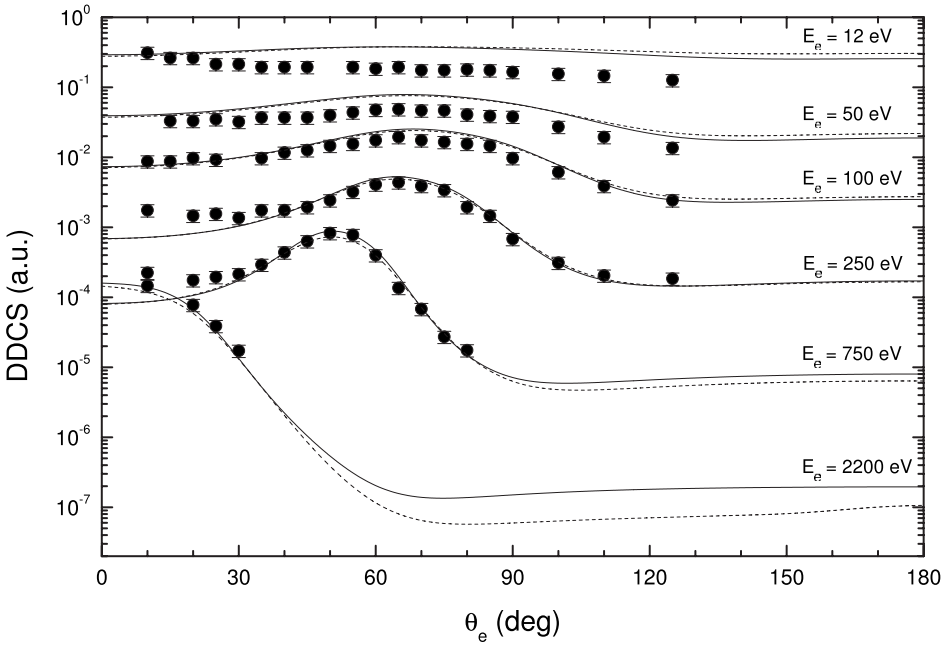

FIG. 3. Same as in Fig. 1 for 1 MeV proton impact.

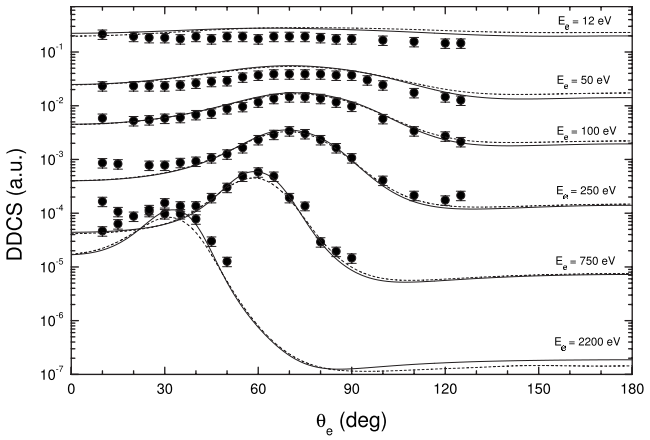

FIG. 4. Same as in Fig. 1 for 1.5 MeV proton impact.

treats the interaction between the scattered proton and the ejected electron. However, when the S factor (Salin factor) [21] is included in the FBA-CW model, an excellent agreement with the data can be observed (except for large values of the ejected angle). In fact, the S factor consists in artificially introducing the mechanism of electron transfer to the continuum, which is written as a multiplicative factor,

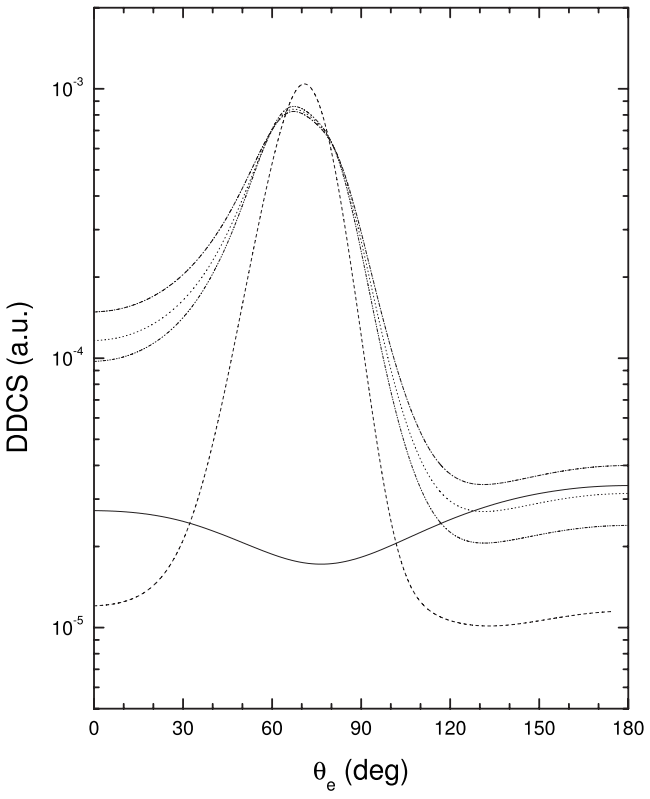

FIG. 5. Doubly differential cross sections for single ionization of water vapor by 1.5 MeV proton impact with the ejection of a 250 eV electron as a function of the electron angle. The calculations are performed in the FBA-CW model for the five molecular subshells of the water target: $^1B_1$ (dash-and-dotted line), $^3A_1$ (dotted line), $^1B_2$ (dash and double dotted line), $^2A_1$ (dashed line), and $^1A_1$ (solid line).

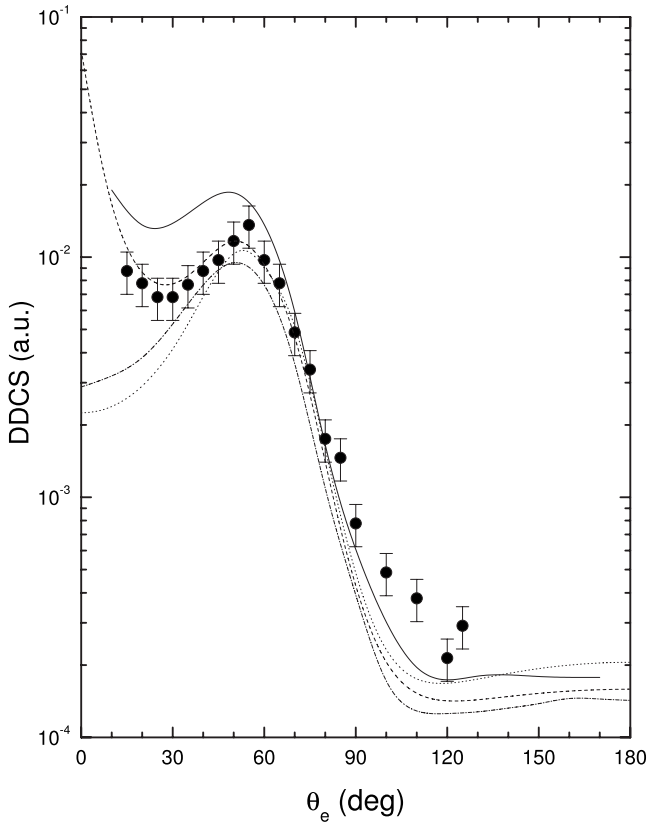

FIG. 6. Doubly differential cross sections for single ionization of water vapor by 0.5 MeV protons impact with the ejection of a 250 eV electron as a function of the ejected electron angle θ_e. The lines correspond to the present different models used: BBK model (solid line), FBA-CW model (dotted line), FBA-CW model with the Salin factor (dashed line), 2CW model (dash and dotted line), whereas the experiments of Toburen and Wilson [5] are represented by solid circles.

$$S = \frac{2\pi/k_{ie}}{1-\exp(-2\pi/k_{ie})}, \tag{21}$$

where $\vec{k}_{ie}=\vec{k}_i/\mu-\vec{k}_e$. Concerning the more sophisticated model (BBK), which is more computer-time consuming, we observe a better agreement for the large ejected angles whereas the DDCS remain overestimated for small values. As a matter of fact, the BBK model exhibits a correct asymptotical Coulomb three-body wave function for the scattered proton and the ejected electron in the residual ion field. Finally, it is important to note that the Salin factor depends on the difference between the velocity of the *incoming proton* and that of the *ejected electron*, whereas in the BBK model this is the difference between the velocity of the *scattered proton* and that of the *ejected electron*. Interestingly, the domain of small values of the momentum transfer means that $\vec{k}_s \approx \vec{k}_i$, as in the present case.

In Fig. 7, we present a comparison between the DDCS calculated in present theoretical models and the experimental measurements for an incident proton energy of 0.3 MeV and an ejected electron of 100 eV [5]. Also included in this figure are the cross sections predicted by the CDW-EIS model

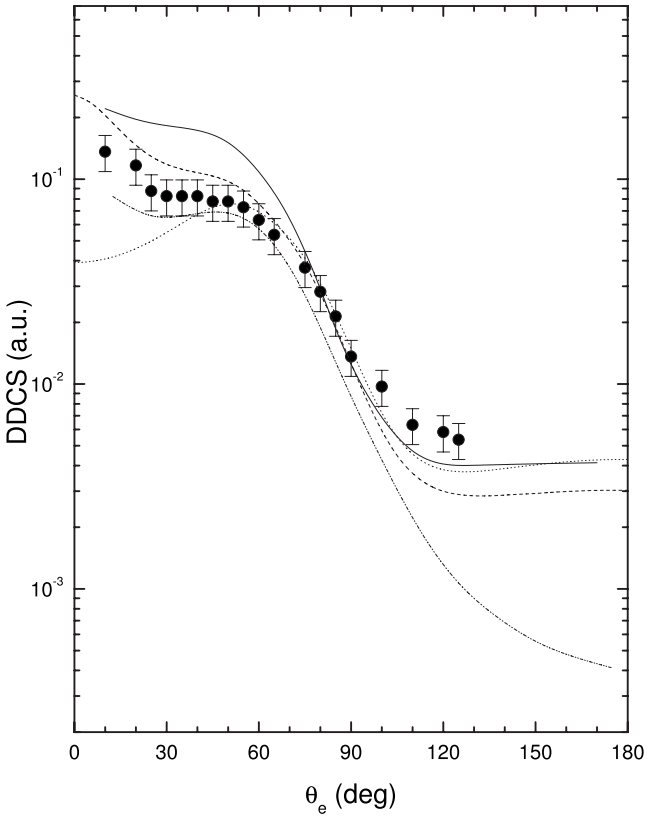

FIG. 7. Doubly differential cross sections for single ionization of water vapor by 0.3 MeV protons with the ejection of a 100 eV electron as a function of the ejected electron angle θ_e. The lines correspond to the different models used: present BBK model (solid line), present FBA-CW model (dotted line), present FBA-CW model with the Salin factor (dashed line), CDW-EIS model [22,23] (dash-dot-dotted line), whereas the experiments of Toburen and Wilson [5] are represented by solid circles.

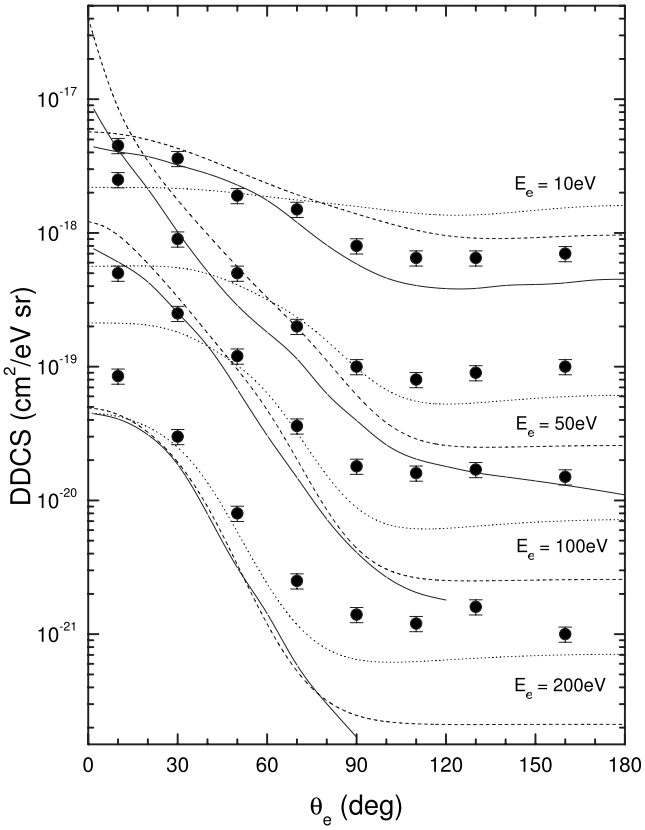

FIG. 8. Doubly differential cross sections for single ionization of water vapor by 0.1 MeV protons with different ejected electron energies as a function of the electron angle θ_e. The experimental results of Bolorizadeh and Rudd [9] (solid circles) are compared to the theoretical results obtained in the present FBA-CW model without the Salin factor (dotted line), in the present FBA-CW model with the Salin factor (dashed line), and in the FBA-CW model of Senger with the Salin factor (solid line).

[22,23]. As before, the FBA-CW model is unable to explain the rapid rise of the DDCS for small ejected angles. But when this model is artificially corrected with the introduction of the Salin factor, it nearly agrees particularly for small angles. Concerning the BBK model, it overestimates the DDCS for small angles but gives a better agreement for large ejected angles. The CDW-EIS model, on the other hand, shows good agreement with the experimental data for small angles but underestimates the DDCS for large angles. This disagreement could be corrected within the framework of the CDW-EIS approximation for atomic targets [29] by using Hartree-Fock bound and continuum states obtained from the numerical integration of the time-dependent Schrödinger equation with model potentials. However, it is important to notice that the calculations performed in the CDW-EIS model used CNDO wave functions for the bound state of the water molecule, in which the molecular orbitals are given as linear combinations of atomic orbitals of the constituents.

In Fig. 8, we are interested in water ionization by low-energy proton impact, namely an incident energy of 100 keV. The experimental measurements of Bolorizadeh and Rudd [9] are compared to the present results obtained in the different models. We observe that the agreement is quite good in the FBA-CW model, relatively better at large ejected angles than at small ejected angles for ejected electron energies of 200, 100, 50, and 10 eV. However, the agreement remains insufficient in all cases. Concerning the "modified" FBA-CW model (with the Salin factor), it also gives the same trends. In addition, we have included in this figure the results obtained by Senger *et al.* [15,16] in the FBA-CW model (with the Salin factor) by using the CNDO representation of the water molecule: a very poor agreement is obtained for ejected angles greater than 90°. So, it is worthwhile to underline the importance of the description of the target by an accurate wave function, especially at large ejected energies and large ejection angles (see, for instance, the differences between the results of the two FBA-CW models). However, we notice that the experimental results for this low incident energy (100 keV) are not correctly reproduced by any of the first-order Born models used here and the use of the Salin factor is not satisfying since it improves the agreement at the forward angles whereas it worsens the agreement at angles greater than 90°.

B. SDCS calculations

By integration of the DDCS with respect to emission angle, the singly differential cross sections may be obtained.

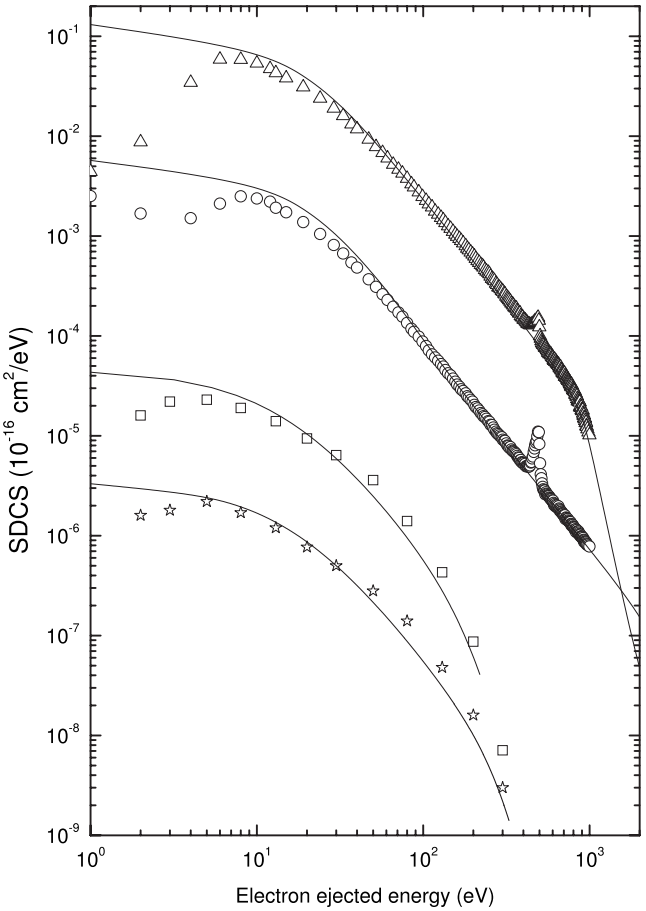

FIG. 9. Singly differential cross sections for ejection of electrons by protons in water vapor as a function of ejected electron energy. Experimental data taken from Toburen and Wilson [5] (open up triangles for 0.5 MeV and open circles for 1.5 MeV) and from Bolorizadeh and Rudd [9] (open squares for 100 keV and open stars for 150 keV). The singly differential cross sections are multiplied by a factor 0.1 for 1.5 MeV and 150 keV for the clarity of the figure.

Figure 9 shows a comparison between the available experimental data [5] and our theoretical results performed in the FBA-CW model. Four values of proton energy have been considered: 1.5 MeV, 0.5 MeV, 150 keV, and 100 keV. We observe a good agreement between the experiments and our results especially for ejected electron energies greater than 10 eV. The Auger electron peak is obviously not reproduced since our models include no Auger process. This good agreement is not surprising and has already been shown by Senger [15,16], who provided, by using a FBA-CW model with the Salin factor, SDCS in very good agreement with the data of Bolorizadeh and Rudd [9]. However, let us note that this S factor plays no important role for the present SDCS calculations since no differences are observed between our results and those of Senger. Finally, it is worth noting that the calculations performed by Vriens in the binary-encounter approximation (BEA) [36] largely overestimate the cross sections in the low-energy region (see [9] for more details).

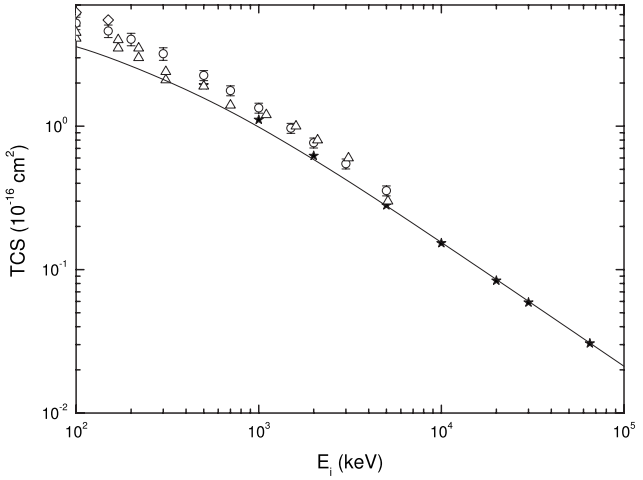

FIG. 10. Total cross sections as a function of the incident energy. Experimental data are taken from various sources: Rudd *et al.* (open circles [7], open up triangles [40]) and Bolorizadeh *et al.* (open diamonds [9]). The theoretical results of Gervais *et al.* (solid stars [39]) are also reported for comparison.

C. TCS calculations

Total ionization cross sections are reported in Fig. 10. We observe that our model (FBA-CW) is able to reproduce with a reasonable agreement the existing experimental data taken from different sources [7,9,40] and provides an excellent agreement with the theoretical results of Gervais *et al.* [39]. However, let us note that the present first Born model becomes invalid for proton energies lower than 100 keV.

IV. CONCLUSION

In the present work, theoretical calculations of doubly differential, singly differential, and total cross sections for the ionization of water vapor by proton impact are compared to a very large set of experimental data.

It has then been clearly observed that the FBA-CW or the DPWBA model was able to reproduce a major part of the existing experimental data for the proton incident energy 0.1–100 MeV at ejected electron energies greater than 10 eV. Moreover, we have underlined the necessity to have an *accurate description of the initial state of the target* since our FBA-CW model generally gives a better agreement than that of Senger, which does not include a good description of the initial state.

Furthermore, we have demonstrated that a sophisticated model, like the BBK model, is needed when the velocity of the ejected electron is close to that of the scattered proton.

Generally speaking, few experimental data exist and we hope that this work opens the way to new experiments. It is now possible to make fully differential cross section measurements (see, for example, Schulz *et al.* [37]) that consist in detecting simultaneously the ejected electron *and* the scattered proton in or out of the plane of the collision. This kind of experiment gives the most accurate information about the mechanism of the ionization (Maydanyuk *et al.* [38]) and will be very interesting to do for water vapor.

ACKNOWLEDGMENTS

We are very grateful to Professor A. C. Roy for many fruitful discussions and comments about this work. The authors would like to thank the CINES (Centre Informatique National de l'Enseignement Supérìeur) of Montpellier (France) for free computer time.

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