Ionization of the cytosine molecule by protons: *Ab initio* calculation of differential and total cross sections

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We present both differential and total cross sections for the direct ionization of the cytosine molecule by protons in the incident energy range 0.1–100 MeV. We have used the first Born approximation and included the pairwise Coulomb interactions of the ejected electron with both the scattered proton and the residual ionized target. In this model, the ground state of the cytosine molecule is described by means of an accurate one center molecular wave function.

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I. INTRODUCTION

Ionization of atoms and molecules by fast charged particles (ions) is of prime importance in plasma physics, radiation physics, and in the study of penetration of charged particles through matter [1–3]. Moreover, the problem of intracellular irradiation of biological structures by ejected electrons is fundamental because low-energy electrons are the principal cause of destructive changes in biological structures at the molecular level. In this case, genetic macromolecules are the basic target. Cytosine ($C_4H_5N_3O$) is one of the simplest pyrimidine bases and is a component of the deoxyribonucleic (DNA) and ribonucleic (RNA) acids.

Until now, there have been no experimental data for the ionization of cytosine by ions. But recently, such an experiment for the ionization of the uracil molecule by protons has been performed [4]. Moreover, total cross section for the ionization of cytosine by electrons has also been measured by Shafranyosh *et al.* [5]. These results indicate that experiments on the ionization of the cytosine molecule by ions will be made possible soon.

Ab initio calculations for the ionization of molecules by ions are extremely scarce, except for the particular case of H_2. In the case of the ionization of pyrimidine bases by ions there are no ab initio calculations. We only can refer the work of Mozejko and Sanche [6] on the ionization of DNA and RNA bases by electrons. These authors have used the simple binary-encounter-Bethe model (BEB) [7,8] to calculate total cross sections for the ionization of guanine, adenine, thymine, cytosine and uracil by electrons. The BEB model is based on a combination of two earlier models based on Mott and Bethe theories. It only needs the values of the electron binding energy, obtained for instance from usual SCF ab initio calculations. In this crude theory, the wave function which describes the initial state of the pyrimidine base is never used. This theory is limited to the calculation of the singly differential cross section (SDCS) and the total cross section (TCS) and is unable to calculate the double differential cross sections (DDCS).

Another approach to treat this problem is the use of the well-known classical trajectory Monte Carlo (CTMC) method which was successfully employed to study ion-(di) atom collisions [9,10]. This model is able to generate DDCS, SDCS, and TCS cross sections while taking into account the forces acting on an electron. These forces have been derived by an accurate evaluation of the electron-proton and electron-molecule interactions [4]. We also notice that the multicenter feature of the molecule is also considered here. However, this model is classical and gives an unexplained peak at 22 eV [4] for the DDCS while the experiments show no maximum.

Recently Abbas *et al.* [11] have developed a model which combines two classical methods: the CTMC and the classical over-barrier (COB) model. Nevertheless this model is able to yield only total cross sections for single ionization, single capture, double ionization and double capture.

One of the basic difficulties in describing the ionization process in ion-molecule collisions by quantum theory arises from the description of the molecular states of the target. Three different techniques can be used to solve this problem. The first one, called Bragg's additivity rule, which consists in expressing each molecular cross sections as a linear combination of atomic cross sections weighted by the number of atoms in the molecule (Olivera *et al.* [12] and Galassi *et al.* [13]). In the second one, called complete neglect of differential overlap (CNDO), the molecular orbitals are written in terms of atomic orbitals of the atomic constituents (Senger and Rechenmann [14] and Senger [15]). The third one uses the molecular orbitals constructed from a linear combination of atomic orbitals in a self-consistent field (MO-LCAO-SCF) (Scherr [16]). This last approach has been commonly used in our previous works for treating the ionization of water by light ion impact (Boudrioua *et al.* [17] and Champion *et al.* [18]). As a matter of fact the FBA-CW model used by Boudrioua *et al.* [17] for the ionization of the water molecule by protons or by α particles [18] is able to yield DDCS, SDCS, and TCS without any parameter. This theory needs an accurate description of the initial state given by one center

molecular wave function. In the case of water molecule such a wave function is available and was provided by Moccia [19]. However, for any pyrimidine base there are no available one-center wave functions. Such a wave function is obtained here, as described below. Then we have been able to apply the same model (FBA-CW) for the case of the ionization of cytosine. The proposed methodology can easily be extended to investigate other molecules.

In Sec. II we present our theoretical model to describe the ionization of a molecule by ions. Then, in Sec. III, the results for the DDCS, SDCS, and TCS are discussed. Finally, conclusions about the modeling of the ionization of molecules by ion impact will be outlined. Atomic units are used throughout unless otherwise indicated.

II. THEORY

Let us first consider the first Born approximation, which is, generally speaking, regarded as valid for an ionization process of a neutral target if the ratio $\frac{Z}{v} \ll 1$ [20], where Z and v are the charge of the incoming particle and the velocity of the incoming particle, respectively. In our case (ionization by proton impact) the incident energy must be greater or equal to 30 keV.

The single ionization of the cytosine molecule by a proton is written as

$$C_4H_5N_3O + p \rightarrow C_4H_5N_3O^+ + p + e^-. \tag{1}$$

The fourfold differential cross section for this process is given by (Massey and Mohr [21])

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

Here the proton has a charge $z_p=1$, a mass μ, an initial momentum $\vec{k}_i$, and the incident energy is $E_i=\frac{k_i^2}{2\mu}$. The final state of the system is 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 is differential in the energy of the ejected electron $\frac{k_e^2}{2}$, differential in the direction of the ejected electron $d\Omega_e$, differential in the energy of the scattered proton $\frac{k_s^2}{2\mu}$, and differential in the direction of the scattered particle $d\Omega_s$. I_i is the ionization energy (*i.e.* the binding energy of the molecular subshell ionized) and $M_{\rm ion}$ denotes the mass of the residual cytosine ion. In Eq. (2) $\vec{K}=\vec{k}_i-\vec{k}_s$ is the momentum transferred from the incident proton to the cytosine target.

If the scattered proton is not detected, the doubly differential cross section (DDCS) for the distribution of the ejected electron is obtained by integration over the energy and the solid angle of the scattered proton:

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

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). So we can neglect the term $\frac{(\vec{K}-\vec{k}_e)^2}{2M_{\rm ion}}$ in the delta function of Eq. (3) and get

$$\frac{d^2\sigma}{d\Omega_e dE_e} = \frac{\mu k_e}{k_i}\int |T_{\rm fi}|^2 \delta\left(\frac{k_i^2}{2\mu} - |I_i| - \frac{k_s^2}{2\mu} - \frac{k_e^2}{2}\right) d\vec{k}_s. \tag{4}$$

When the scattered proton and the ejected electron are detected in coincidence, the triple differential cross section (TDCS) is defined by

$$\frac{d^3\sigma}{d\Omega_e d\Omega_s dE_e} = \mu^2 \frac{k_e k_s}{k_i}|T_{\rm fi}|^2. \tag{5}$$

Such difficult experiments have become available only in recent years [22,23].

The scattering amplitude is given by

$$T_{\rm fi} = -\frac{1}{2\pi}\langle \Psi_f | V | \Psi_i \rangle, \tag{6}$$

where V represents the interaction between the incoming proton and the target. The initial state of the system consisting of the incoming proton and the cytosine molecule is then described by the product of a plane wave which represents the incident particle and the ground state wave function of the target molecule

$$|\psi_i\rangle = |\phi(\vec{k}_i, \vec{r}_0)\varphi_i(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{58})\rangle, \tag{7}$$

where $\vec{r}_i$ denotes the position vector of the ith bound electron of the target with respect to the center of the molecule and $\vec{r}_0$ that of the passing proton with respect to the center of the molecule.

The cytosine wave function has been obtained using a relatively simple *ab initio* scheme together with the GAUSSIAN03 program [24]. The geometry of the molecule has been optimized at the MP2/6-31G(d) computational level, where MP2 stands for electronic correlation energy calculations using second-order perturbation theory (post-Hartree-Fock approach) and 6-31G(d) stands for a standard Pople's basis set (it includes Gaussian-type orbitals, a double-zeta valence shell, and polarization orbitals on nonhydrogen atoms). The molecular orbitals hereafter correspond to the Hartree-Fock calculations with the basis set. The multicenter wave function is then converted to a single-center expansion of usual Slater-type functions by using partial-wave expansion techniques [25,26]. In our study we neglect the ionization of the 16 inner shell electrons. This approximation is usual in the present case of impact energy because an inner shell electron is unlikely to have a significant emission probability than the outer one. In fact, we have checked this ap-

proximation in our previous DDCS study of the ionization of the water molecule by protons [17] and found that the contribution of the inner shell electrons is generally very weak except for large values of the ejected angles.

The 21 one-center molecular wave functions $v_j(\vec{r})$ (with j ranging from 1 to 21), containing the 42 valence electrons, are expressed by linear combinations of Slater-type functions and are written as

$$v_j(\vec{r}) = \sum_{k=1}^{N_j} a_{jk} \Phi^{\xi_{jk}}_{n_{jk} l_{jk} m_{jk}}(\vec{r}), \tag{8}$$

where N_j is the number of Slater functions used in the construction of the jth molecular orbital and a_{jk} the weight of each complex atomic component $\Phi^{\xi_{jk}}_{n_{jk} l_{jk} m_{jk}}(\vec{r})$. In Eq. (8), $\Phi^{\xi_{jk}}_{n_{jk} l_{jk} m_{jk}}(\vec{r})$ is written as

$$\Phi^{\xi_{jk}}_{n_{jk} l_{jk} m_{jk}}(\vec{r}) = [R^{\xi_{jk}}_{n_{jk}}(r) + iS^{\xi_{jk}}_{n_{jk}}(r)] Y^{m_{jk}}_{l_{jk}}(\hat{r}), \tag{9}$$

where the radial part $[R^{\xi_{jk}}_{n_{jk}}(r) + iS^{\xi_{jk}}_{n_{jk}}(r)]$ is given by the usual radial Slater-type functions. We notice that here the wave function is generally complex whereas it was real in the case of Moccia' wave functions [19].

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

$$|\psi_f\rangle = |\psi_{f1} \psi_{f2}\rangle, \tag{10}$$

where ψ_{f1} describes the system constituted by an ejected electron and a scattered proton, whereas ψ_{f2} describes the 41 bound electrons of the target. The so-called frozen-core approximation supposes that the ion is described by the same single-particle basis (8) and (9) as in the case of the neutral cytosine molecule. This model allows reducing the molecular problem with 42 bound electrons to the two-body problem with only one active electron. Such a simplification leads to scattering amplitude given by

$$T = -\frac{z_P}{2\pi} \left\langle \psi_f(\vec{k}_s, \vec{r}_0, \vec{k}_e, \vec{r}_1) \left| \frac{1}{|\vec{r}_0 - \vec{r}_1|} - \frac{1}{r_0} \right| \phi(\vec{k}_i, \vec{r}_0) v_j(\vec{r}_1) \right\rangle. \tag{11}$$

It is important to note that these wave functions $v_j(\vec{r}_1)$ correspond to a particular orientation of the molecular target given by the Euler angles (α, β, γ) [27,28]. Thus, the differential cross sections we have calculated correspond in fact to the ionization of an oriented cytosine molecule. Under these conditions, we need to average these differential cross sections in order to compare with experiment. The averaging is accomplished by an analytical integration over the Euler angles, owing to the property of the rotation matrix [27,28]. This procedure is followed for each of the 21 valence orbitals of the cytosine molecule and the differential cross sections presented here correspond to "global" differential cross sections obtained by summing up all the (outer) subshell contributions weighted by the number N_{elec} of electrons per orbital, i.e., $N_{\text{elec}}=2$.

In the present FBA-CW model the scattered proton is described by a plane wave, whereas the ejected electron is described by a Coulomb wave

$$\psi_{f_1}(\vec{k}_s, \vec{r}_0, \vec{k}_e, \vec{r}_1) = \exp(i\vec{k}_s \cdot \vec{r}_0) \varphi_c(\vec{k}_e, \vec{r}_1), \tag{12}$$

with

$$\varphi_C(\vec{k}_e, \vec{r}_1) = \frac{\exp(i\vec{k}_e \cdot \vec{r}_1)}{(2\pi)^{3/2}} {}_1F_1[-iZ_e/k_e, 1, -i(\vec{k}_e \cdot \vec{r}_1 + k_e r_1)] \times \exp\left(\frac{\pi Z_e}{2k_e}\right) \Gamma(1 + iZ_e/k_e). \tag{13}$$

The effective ionic charge Z_e is taken to be equal to 1 (Brothers and Bonham [29]). Using Eqs. (8), (9), (12), and (13) in Eq. (11), the scattering amplitude T is evaluated with the help of analytical formulas of Dal Cappello *et al.* [30]. Finally, DDCS given in Eq. (4) is computed after performing the integration over $d\Omega_s$ numerically.

When the velocity of the ejected electron is close to that of the scattered proton the 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, called charge transfer to the continuum (ECC), corresponds to the classical Thomas effect [31] of capture. The ECC process can be included easily in the calculations by introducing the multiplicative Salin factor S [32] in Eq. (4)

$$S = \frac{2\pi/\gamma}{1 - \exp(-2\pi/\gamma)}, \tag{14}$$

where $\gamma = \frac{1}{\sqrt{k_{ie}}} - \frac{\mu}{k_i}$ and $\vec{k}_{ie} = \frac{\vec{k}_i}{\mu} - \vec{k}_e$.

III. RESULTS AND DISCUSSION

To date there are no measurements on the ionization of the cytosine molecule by proton impact. However, such an experiment has been recently performed on the uracil molecule [4] and we believe that experiments on cytosine can be made in the near future. So we decided to investigate the ionization of the cytosine molecule for the same kinematics as those adopted in the experimental study of the ionization of water [33–41] and uracil [4] molecules.

Doubly differential cross sections. Figure 1 shows the results of two FBA-CW models: the first with the Salin factor, and the second without this factor. The DDCS is drawn as a function of the electronic energy for a fixed angle of 35° with respect to the beam direction. The incoming energy is 100 keV, as that used in the study of the ionization of the uracil molecule by protons [4]. We find that the DDCS decreases with the increase in the energy of the ejected electron. We notice no maximum as was observed by the authors of Ref. [4] when they apply their CTMC model. Thus we demonstrate that our model is able to reproduce the experimental shape observed in the case of uracil, contrary to the CTMC model which gives a maximum for an ejected energy of 22 eV. We also notice that the Salin factor is not negligible in the present kinematics except for values of the electronic energies greater than 140 eV. It is worth noting that in the present case, the speed of the incoming proton is about 2 a.u., which corresponds to a kinetic energy for the ejected electron of 54.4 eV and this is why the S factor is important here.

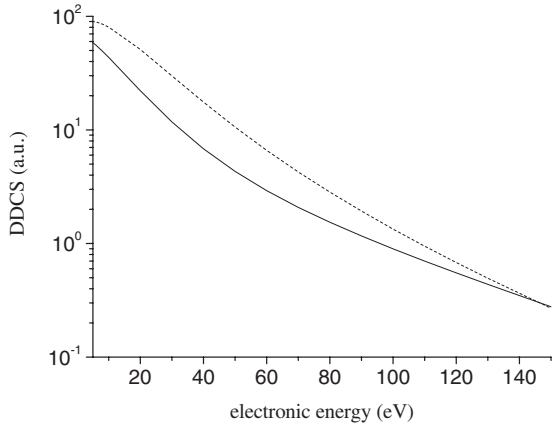

FIG. 1. Doubly differential cross sections for single ionization of the cytosine molecule by 100 keV protons for an angle of 35° as a function of the electron energy. Theory: the solid line represents the FBA-CW model without the Salin factor, whereas the dashed line is the FBA-CW model with the Salin factor.

Figures 2, 3, and 4 show the results of our FBA-CW model with the S factor at incident energies of 0.1, 0.5, and 1.5 MeV, respectively. The choice of these incident energies correspond to those used in experiments on the water molecule [33–37]. A big rise of the DDCS is found for small ejection angles at an incident energy of 0.1 MeV and an electron energy of 50 eV (Fig. 2) which corresponds to nearly the same speed of the incoming particle. This big rise is due to the process of charge transfer to the continuum which becomes important when the velocity of the scattered particle and that of the ejected electron are close. We find analogous results for an incident energy E_i=0.5 MeV and an ejection energy E_e=250 eV (Fig. 3), also for E_i=1.5 MeV and E_e=750 eV (Fig. 4).

A comparison of our results with those found in the same model (FBA-CW with S factor) used for the study of the ionization of water by protons shows that the shapes are very similar but the magnitude of these DDCS does not depend of the number of electronic states included in our calculations. For instance, we find ratios close to 15, 12, 2.2, and 5 for

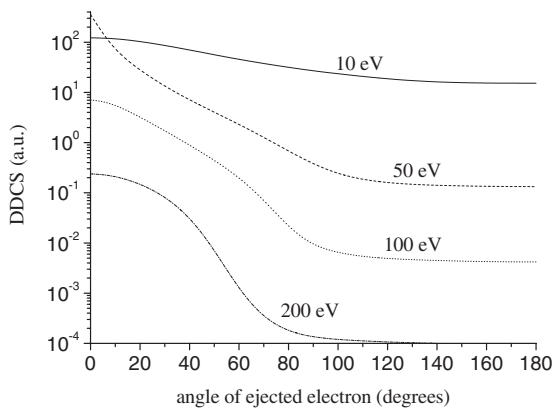

FIG. 2. Doubly differential cross sections for single ionization of the cytosine molecule by 100 keV protons for different electron energies as a function of the electron angle. Theory: FBA-CW model with the Salin factor.

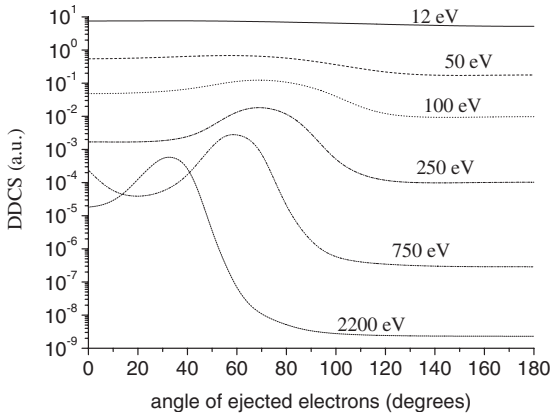

FIG. 3. Same as in Fig. 2 for 500 keV proton impact.

electron energies of 10, 50, 100, and 200 eV, respectively, while the ratio of the number of electronic states considered is 21/4.

In Fig. 4 we notice that the maximum of the DDCS corresponds to the values of θ_e such as

$$\cos\theta_e \approx \frac{k_e\mu}{2k_i} \tag{15}$$

when the electron ejected energy is 100, 250, 750, and 2200 eV, respectively. These maxima result from a particular value of the momentum transfer

$$|\vec{K}| = |\vec{k}_i - \vec{k}_s| = k_e \tag{16}$$

and are near to 78°, 72°, 60°, and 34°, respectively. In this case the collision is seen as a binary process in which the energy lost by the incident proton is transferred to the target molecular electron, while the residual ion is acting as a spectator [42,43]. We obtain Eq. (15) from the conservation of the energy

$$\frac{k_i^2}{2\mu} - |I_i| - \frac{k_s^2}{2\mu} - \frac{k_e^2}{2} - \frac{(\vec{K}-\vec{k}_e)^2}{2M_{ion}} = 0,$$

then by neglecting the terms $|I_i| + \frac{(\vec{K}-\vec{k}_e)^2}{2M_{ion}}$ we finally get

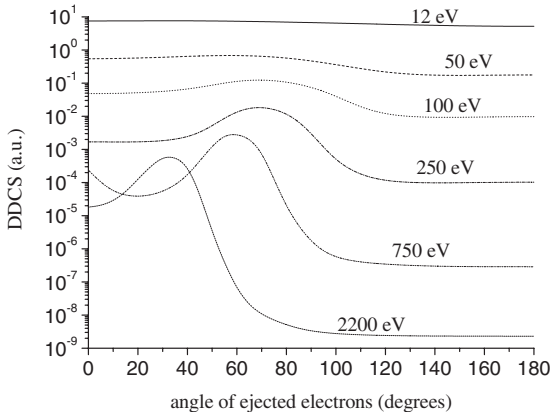

FIG. 4. Same as in Fig. 2 for 1.5 MeV proton impact.

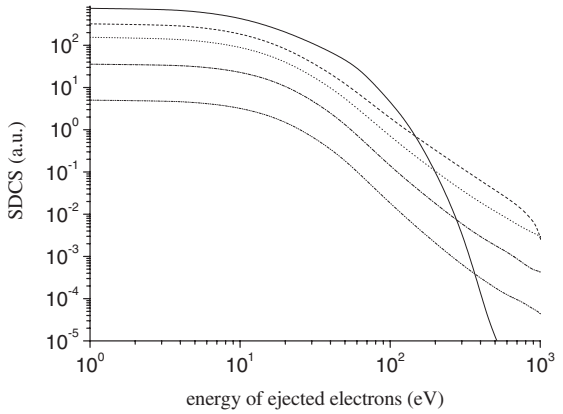

FIG. 5. Singly differential cross sections (SDCS) for ejection of electrons by protons from cytosine molecule as a function of ejected electron energy. Theory: FBA-CW model with the Salin factor. Solid line: SDCS for 100 keV proton impact, dashed line: SDCS for 500 keV proton impact, dotted line: SDCS for 1500 keV proton impact, dash-dotted line: SDCS for 10 MeV proton impact and dash-dot-dotted line: SDCS for 100 MeV proton impact.

$$\frac{k_i^2}{2\mu} - \frac{k_s^2}{2\mu} - \frac{k_e^2}{2} = 0. \tag{17}$$

With the help of Eq. (16) we arrive at

$$\frac{k_i^2}{2\mu} - \frac{(k_i^2 - 2k_i k_e \cos(\theta_e) + k_e^2)}{2\mu} - \frac{k_e^2}{2} = 0$$

and by neglecting $\frac{k_e^2}{2\mu}$ we obtain Eq. (15).

Singly differential cross sections. By integration of the DDCS with respect to emission angle, the singly differential cross sections can be obtained as a function of the electron ejected energy. Figure 5 shows the results of our FBA-CW model including the S factor for five values of proton energy: 100, 500, 1500 keV, 10 and 100 MeV. We see that the shapes of the SDCS are similar to those obtained in the case of the ionization of water by protons. Generally speaking, the SDCS decreases as the incident energy is increasing, except for large values of the electron ejected energy (greater than 100 eV). We notice that the SDCS for 100 keV decreases fast from an energy of the ejected electrons close to 200 eV. This particular value corresponds to the maximum of energy that can be transferred to a free electron by the projectile. From Eq. (17) and with $k_i = k_s + k_e$ Eq. (16) we get $\frac{k_i^2}{2\mu} - \frac{(k_i - k_e)^2}{2\mu} - \frac{k_e^2}{2} = 0$ and $k_e = \frac{2k_i}{1+\mu} \approx \frac{2k_i}{\mu}$. The energy transferred to the electron is then $\Delta E = \frac{k_i^2}{2\mu} - \frac{k_s^2}{2\mu} = \frac{k_e^2}{2} \approx \frac{4E_i}{\mu}$. For our case (100 keV) we find $\Delta E \approx 217$ eV. For 500 keV the maximum of the energy transferred to the electron is found for 1087 eV.

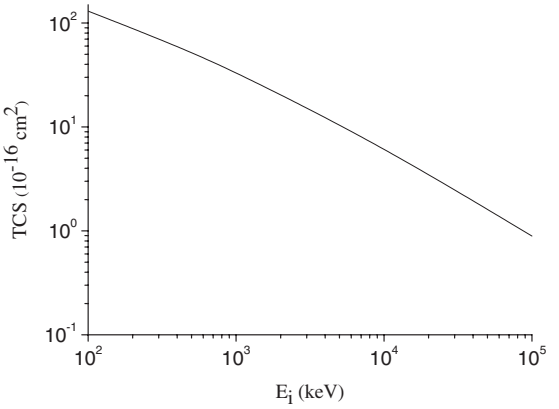

FIG. 6. Total cross section as a function of the incident energy. Theory: FBA-CW model with the Salin factor.

Total cross sections. By integrating of the SDCS with respect to the energy of the ejected electron the total cross section (Fig. 6) can be obtained as a function of the incident energy. If we compare our results to those of Boudrioua *et al.* [17] for the total cross section of the ionization of water by protons we see that the shapes are similar but the ratio of these two cross sections is close to 38. Hence the ratio does not depend of the number of electronic states included in our calculations.

IV. CONCLUSION

The theoretical results of doubly differential, singly differential and total cross section have been presented and discussed. These results can now be used for future experiments about the ionization of the cytosine molecule by protons. Our *ab initio* model (FBA-CW), which was able to reproduce a major part of the experimental data in the case of the ionization of water by protons, is expected to be valid for proton incident energy 0.1–100 MeV at ejected electron energies greater than 10 eV. The capture of the ejected electron in the continuum (ECC) has been included in our model by using the factor of Salin [32].

We hope that this work opens the way to new experiments, especially for fully differential cross sections [21] that consist in detecting simultaneously the ejected electron and the scattered proton. Since this kind of difficult experiment gives the most accurate information about the mechanism of the ionization of an atom or a molecule an extensive knowledge of this mechanism is essential for the study of penetration of charged particles through biological structures.

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[1] H. A. Bethe, Ann. Phys. **5**, 325 (1930).
[2] U. Fano, Annu. Rev. Nucl. Sci. **13**, 1 (1963).
[3] M. Inokuti, Rev. Mod. Phys. **43**, 297 (1971).
[4] P. Moretto-Capelle and A. Le Padellec, Phys. Rev. A **74**, 062705 (2006).
[5] I. Shafranyosh, M. I. Sukhoviya, and M. I. Shafranyosh, J. Phys. B **39**, 4155 (2006).
[6] P. Mozejko and L. Sanche, Radiat. Environ. Biophys. **42**, 201 (2003).
[7] Y. K. Kim and M. E. Rudd, Phys. Rev. A **50**, 3954 (1994).
[8] W. Hwang, Y. K. Kim, and M. E. Rudd, J. Chem. Phys. **104**, 2956 (1996).
[9] R. E. Olson, Phys. Rev. A **27**, 1871 (1983).
[10] R. E. Olson, J. Ullrich, and H. Schmidt-Böcking, Phys. Rev. A **39**, 5572 (1989).
[11] I. Abbas, C. Champion, B. Zarour, B. Lasri, and J. Hanssen, Phys. Med. Biol. **53**, N41 (2008).
[12] G. H. Olivera, A. E. Martinez, R. D. Rivarola, and P. D. Fainstein, Radiat. Res. **144**, 241 (1995).
[13] M. E. Galassi, R. D. Rivarola, M. Beuve, G. H. Olivera, and P. D. Fainstein, Phys. Rev. A **62**, 022701 (2000).
[14] B. Senger and R. V. Rechenmann, Nucl. Instrum. Methods Phys. Res. B **2**, 204 (1984).
[15] B. Senger, Z. Phys. D: At., Mol. Clusters **9**, 79 (1988).
[16] C. W. Scherr, J. Chem. Phys. **23**, 569 (1955).
[17] O. Boudrioua, C. Champion, C. Dal Cappello, and Y. V. Popov, Phys. Rev. A **75**, 022720 (2007).
[18] C. Champion, O. Boudrioua, C. Dal Cappello, Y. Sato, and D. Ohsawa, Phys. Rev. A **75**, 032724 (2007).
[19] R. Moccia, J. Chem. Phys. **40**, 2186 (1964).
[20] J. Ullrich, R. Moshammer, A. Dorn, R. Dörner, L. Ph. H. Schmidt, and H. Schmidt-Böcking, Rep. Prog. Phys. **66**, 1463 (2003).
[21] H. S. W. Massey and C. B. O. Mohr, Proc. R. Soc. London, Ser. A **140**, 613 (1933).
[22] N. V. Maydanyuk, A. Hasan, M. Foster, B. Tooke, E. Nanni, D. H. Madison, and M. Schulz, Phys. Rev. Lett. **94**, 243201 (2005).
[23] M. Schulz, R. Moschammer, D. Fischer, H. Kollmus, D. H. Madison, S. Jones, and J. Ullrich, Nature (London) **422**, 48 (2003).
[24] M. J. Frisch *et al.*, GAUSSIAN 03, Revision B.05, Gaussian, Inc., Wallingford CT, 2004.
[25] K. Kaufmann, W. Baumeister, and M. Jungen, J. Phys. B **22**, 2223 (1989).
[26] H. Hafied, A. Eschenbrenner, C. Champion, M. F. Ruiz-Lopez, C. Dal Cappello, I. Charpentier, and P. A. Hervieux, Chem. Phys. Lett. **439**, 55 (2007).
[27] C. Champion, J. Hanssen, and P. A. Hervieux, Phys. Rev. A **63**, 052720 (2001).
[28] C. Champion, J. Hanssen, and P. A. Hervieux, J. Chem. Phys. **121**, 9423 (2004).
[29] M. J. Brothers and R. A. Bonham, J. Phys. B **17**, 4235 (1984).
[30] C. Dal Cappello, C. Tavard, A. Lahmam-Bennani, and M. C. Dal Cappello, J. Phys. B **17**, 4557 (1984).
[31] L. H. Thomas, Proc. R. Soc. London, Ser. A **114**, 561 (1927).
[32] A. Salin, J. Phys. B **2**, 631 (1969).
[33] L. H. Toburen and W. E. Wilson, J. Chem. Phys. **66**, 5202 (1977).
[34] L. H. Toburen, W. E. Wilson, and R. J. Popowich, Radiat. Res. **82**, 27 (1980).
[35] M. E. Rudd, T. V. Goffe, R. D. DuBois, and L. H. Toburen, Phys. Rev. A **31**, 492 (1985).
[36] M. E. Rudd, A. Itoh, and T. V. Goffe, Phys. Rev. A **32**, 2499 (1985).
[37] M. A. Bolorizadeh and M. E. Rudd, Phys. Rev. A **33**, 888 (1986).
[38] U. Werner, K. Beckord, J. Becker, and H. O. Lutz, Phys. Rev. Lett. **74**, 1962 (1995).
[39] F. Gobet, B. Farizon, M. Farizon, M. J. Gaillard, M. Carré, M. Lezius, P. Scheier, and T. D. Mark, Phys. Rev. Lett. **86**, 3751 (2001).
[40] F. Gobet, S. Eden, B. Coupier, J. Tabet, B. Farizon, M. Farizon, M. J. Gaillard, M. Carré, S. Ouaskit, T. D. Mark, and P. Scheier, Phys. Rev. A **70**, 062716 (2004).
[41] D. Ohsawa, Y. Sato, Y. Okada, V. P. Shevelko, and F. Soga, Phys. Rev. A **72**, 062710 (2005).
[42] M. A. Coplan, J. H. Moore, and J. P. Doering, Rev. Mod. Phys. **66**, 985 (1984).
[43] N. F. Mott and H. S. W. Massey, in *The Theory of Atomic Collisions*, 3rd ed., edited by W. Marshall and D. H. Wilkinson (Clarendon Press, Oxford 1971).