

Single-electron capture in collisions of proton beams with molecules of biological interestM. E. Galassi,¹ P. N. Abufager,¹ P. D. Fainstein,² and R. D. Rivarola¹¹*Instituto de Física Rosario (CONICET-UNR), Avenida Pellegrini 250, 2000 Rosario, Argentina*²*Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, Avenida E. Bustillo 9500, 8400 Bariloche, Argentina*

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Single-electron charge exchange from simple molecular targets of biological interest to fast ion beams is investigated using the continuum-distorted-wave–eikonal-initial-state model. Thus, this model is applied for electron capture from molecules with many orbitals in the fundamental state. The role played by the representation of the initial state is analyzed and contributions from different molecular orbitals to total cross sections are calculated. The results are shown to be in very good agreement with existing experimental data for collision energies larger than a few tens of keV.

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I. INTRODUCTION

The study of electronic reactions produced by the impact of ion beams on molecular targets is of great importance in many areas of physics, for example, in plasma physics, astrophysics, and medical physics. Particular attention has been given in recent years to its application in radiotherapy. It is well known that living matter is composed of liquid water and complex structures like DNA, but also of other molecules such as N₂, O₂, CH₄, CO, and CO₂.

Ionization and capture from O₂ and water vapor in collisions with proton beams have been a subject of our previous research [1–4]. By employing a distorted-wave model, differential and total cross sections as well as stopping power and dose profiles were determined and compared with success with existing experimental data. In recent years, multiple ionization of water by interaction with protons and heavier bare ions has also been investigated [5]. This process has been related to the production of radicals with oxygen excess in biological tissue irradiation [6,7], a process which can lead to the breaking of DNA chains.

Theoretical calculations of single ionization of molecules composed of atoms with small atomic numbers by impact of protons have been also performed [8]. Double-differential cross sections, as a function of the ejected electron linear momentum, and total cross sections were determined by using the continuum-distorted-wave–eikonal-initial-state approximation (CDW-EIS) [9–11]. The analysis of these multielectron systems was reduced to a one-active-electron description where only one electron was assumed to be ionized while all the others in the molecule, the *passive* ones, were supposed to remain as frozen in their initial orbitals. Molecular vibration and rotation were neglected during the collision. The targets were described as a simple collection of the atoms composing the molecule or taking into account their molecular orbitals. Thus, in the first case, cross sections were calculated using the Bragg’s additivity rule, whereas in the second case, the molecular orbitals were constructed from a linear combination of atomic orbitals in a self-consistent field. Consequently double-differential cross sections for each molecular orbital were calculated by making a linear combination of atomic double-differential cross sections with linear coefficients obtained from a population analysis. In general, a very good representation of experiments was obtained, showing however

that the cross sections at intermediate collision energies evidence some sensitivity to the description of the target.

In the present work, the study is extended to single-electron capture by protons impacting on these low-*Z* molecules. Investigations are motivated by the fact that, to our knowledge, a limited number of theoretical and experimental results exist for these systems [12]. A compilation of total cross sections was also given and best fitting curves were determined with an estimated uncertainty of 20% [13]. Moreover, experimental data have been simply obtained as the difference between the positive-ion-production and the electron-production total cross sections, suffering in accuracy when the measured values are close together. Also, in order to avoid discontinuities of the data sets at each energy, least-squares computer fits of mathematical equations [14] were used to obtain the capture total cross sections. Thus, the report of theoretical results obtained with the first-principle model appears as necessary to support the accuracy of measurements and compiled data. In charge exchange it is well known that at least a second-order of the Born series must be considered to describe the reaction for impact energies going from intermediate to high collision velocities. Thus, we have chosen to employ the CDW-EIS approximation, which implicitly contains higher orders of the Born series [15,16]. This model, in a one-active-electron approximation, has been successfully applied to describe electron capture by ion impact on atomic and H₂ targets. The dependence of total cross sections on the description of the molecular target is also analyzed.

Hereafter and throughout the text atomic units are used except where otherwise stated.

II. THEORY

Let us consider the case of a bare nucleus of nuclear charge Z_p impacting on N₂, CH₄, CO, and CO₂ molecular targets. As mentioned previously the many-electron collision system is reduced to a one-active-electron reaction, where the electron is independently captured from different initial orbitals by direct interaction with the projectile. The straight line version of the impact parameter approximation is employed in the calculations. The dynamics of the process is analyzed within the CDW-EIS model. For simplicity we present the main aspects of this model for an atomic target, considering that the molecular orbitals are represented by a linear combination

TABLE I. Population and binding energies of the CH₄ molecular orbitals.

Molecular orbital	Population	Binding energy ε_i (eV)
C 1s	2.00 C 1s	-290.70
2a ₁	1.133 C 2s + 0.867 H 1s	-22.90
1t ₂	3.399 C 2p + 2.601 H 1s	-12.60

of atomic ones. The process is described from a reference frame fixed in the center of mass of the target. Thus, the initial distorted-wave function is chosen as

$$\chi_i^{+,EIS} = \phi_i(\vec{x}) \exp(-i\varepsilon_i t) \exp\left[-i\frac{Z_p}{v} \ln(vs + \vec{v} \cdot \vec{s})\right], \quad (1)$$

with $\vec{x}(\vec{s})$ being the active electron position relative to the target (projectile), $\phi_i(\vec{x})$ the initial orbital wave function with corresponding energy ε_i , and \vec{v} the collision velocity. The eikonal phase in expression (1) describes the electron in an eikonal continuum state of the projectile. The final distorted-wave function is chosen as

$$\chi_f^{-,CDW} = \phi_f(\vec{s}) \exp(-i\varepsilon_f t) \exp\left(i\vec{v} \cdot \vec{x} - i\frac{v^2}{2}t\right) N^*(\xi) \times {}_1F_1(-i\xi; 1; -ivx - i\vec{v} \cdot \vec{x}), \quad (2)$$

where $\phi_f(\vec{s})$ is the final-state bound wave function with energy ε_f , the second multiplicative exponential factor in expression (2) is the Galilean transformation of this bound wave function from the projectile to target reference frame, $\xi = Z_T^*/v$ with Z_T^* being an effective target nuclear charge that takes partially into account the dynamic correlation between the active and the passive electrons, and $N^*(\xi) {}_1F_1(-i\xi; 1; -ivx - i\vec{v} \cdot \vec{x})$ is a Coulomb continuum factor which describes the electron in the residual target with a state density given by $|N(\xi)|^2$.

The molecular orbitals are constructed from a linear combination of atomic orbitals (corresponding to the compounds of the target) in a self-consistent field approximation (MO-LCAO-SCF). The complete neglect of differential overlap method (CNDO) is used for the population analysis of the different molecular orbitals [17]. The contributions of the different atomic states in the molecular orbitals were extracted from Ref. [18] for N₂, Ref. [19] for CH₄, Ref. [20] for CO, and Ref. [21] for CO₂. The electronic configurations for the different targets are (C 1s)²(2a₁)(1t₂)⁶ for CH₄, (N 1s)⁴(σ_g2s)²(σ_u2s)²(π_u2p)⁴(σ_g2p)² for N₂, (O 1s)²(C 1s)²(1σ)²(2σ)²(1π)⁴(3σ)² for CO, and (O 1s)⁴(C 1s)²(3σ_g)²(2σ_u)²(4σ_g)²(3σ_u)²(1π_u)⁴(1π_g)⁴ for CO₂.

 TABLE II. Population and binding energies of the N₂ molecular orbitals.

Molecular orbital	Population	Binding energy ε_i (eV)
N 1s	4.00 N 1s	-409.90
σ _g 2s	2.00 N 2s	-37.23
σ _u 2s	2.00 N 2s	-18.60
π _u 2p	4.00 N 2p	-16.80
σ _g 2p	2.00 N 2p	-15.50

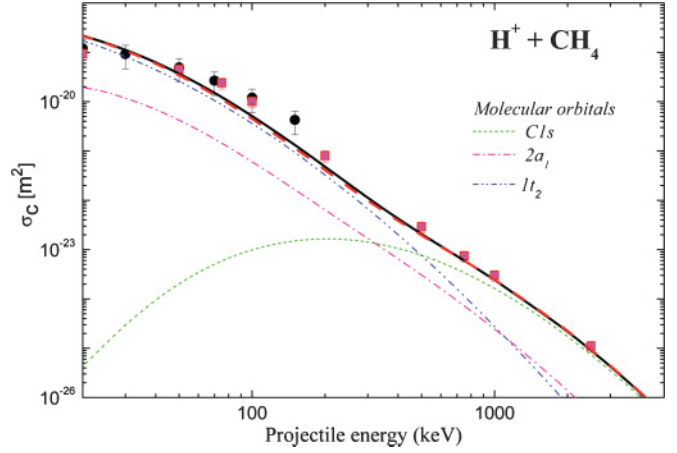


FIG. 1. (Color online) TCS for single-electron capture of CH₄ by proton impact as a function of the projectile energy. Contributions from the different molecular orbitals are shown. Theory: solid line (black online), MO-LCAO-SCF; dashed line (red online), Bragg's rule; Experiments: circles, from [12]; squares, from [13].

The corresponding information is given in Tables I to IV. Experimental orbital energies ε_i are considered in the calculations and the effective parameter employed for the different atomic states is taken as $Z_T^* = \sqrt{-2n\varepsilon_i}$, with n being the principal quantum number of the corresponding atomic wave function.

III. RESULTS AND DISCUSSIONS

Total cross sections for single-electron charge exchange from CH₄, N₂, CO, and CO₂ molecules to proton beams calculated within the CDW-EIS approximation are presented in Figs. 1 to 4. In order to analyze the influence of the molecular representation on the total cross sections for the different targets, results obtained using the MO-LCAO-SCF description of the molecular orbitals are compared with calculations obtained employing Bragg's additivity rule. In both cases the atomic orbitals are described with the Roothaan-Hartree-Fock approximation [22]. Since the pioneering theoretical [23,24] and experimental [25,26] works on electron capture from hydrogen molecules, it is well known that differential cross

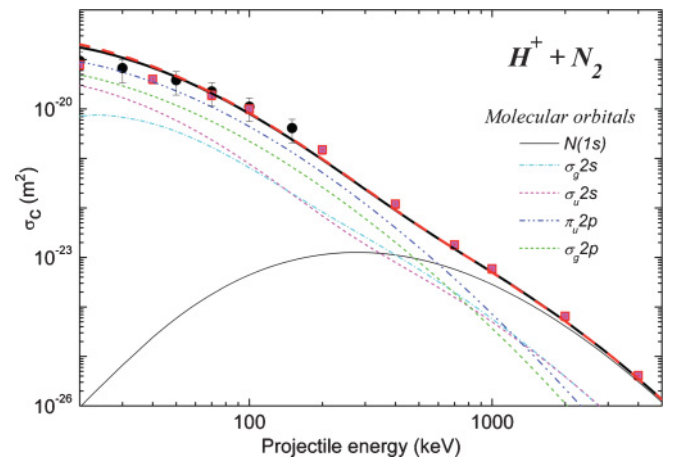


FIG. 2. (Color online) Same as Fig. 1, but for proton impact on N₂.

TABLE III. Population and binding energies of the CO molecular orbitals.

Molecular orbital	Population	Binding energy ε_i (eV)
O 1s	2.00 O 1s	-542.1
C 1s	2.00 C 1s	-295.9
1 σ	1.207 O 2s + 0.178 O 2p + 0.333 C 2s + 0.282 C 2p	-38.3
2 σ	0.627 O 2s + 0.985 O 2p + 0.386 C 2s + 0.002 C 2p	-20.1
1 π	2.980 O 2p + 1.020 C 2p	-17.2
3 σ	1.207 O 2s + 0.178 O 2p + 0.333 C 2s + 0.282 C 2p	-14.5

sections depend on the molecular orientation. So, the use of more elaborated descriptions of the orbitals considering the molecular structure appears to be necessary. However, after averaging on the molecular orientations and integrating on the projectile scattering angle in order to obtain total cross sections, at high enough impact energies the molecular structure is expected to play a minor role. Very recently, by using CNDO and molecular descriptions [27] of the initial orbitals, it has been proven that single-capture total cross sections for impact of protons, α particles, and C^{6+} ions on water targets are not sensitive to the molecular character of the wave function [28].

The contributions of electron capture to projectile states with principal quantum numbers $n = 1$ and 2 are considered in the present calculations. In fact, we have verified that the contribution of capture to the $n = 1$ projectile ground state is much larger than to the $n = 2$ excited projectile bound states and that contributions from capture to $n = 3$ are negligible. Total cross sections using MO-LCAO-SCF descriptions are very close to those obtained employing the simpler Bragg's rule for the corresponding molecules.

We note that the validity of the CDW-EIS approximation is restricted to impact energies larger than some tens of keV. In this range, the CDW-EIS model presents a very good agreement with experiments. Some overestimation of measurements is obtained at intermediate collision energies for CH_4 . However, it must be noted that some limitation in the accuracy of the experimental data has been reported [12]. The contributions to total cross sections from different molecular

orbitals are also studied. As is well known from atomic targets, electron capture is preferably produced at impact velocities close to the mean orbital velocities of the active electron. Thus, at high collision energies charge exchange is produced from the inner orbitals, which correspond to K -shell states of the atomic compounds of the molecules (see for example in Figs. 1 and 2 the cases of CH_4 and N_2). It is interesting to note that inner shell contributions produce a smooth change in the slope of total cross sections which is observed in both the theoretical calculations and the recommended data.

For CO_2 , the preference of capture from O 1s (with a binding energy of -297.5 eV) with respect to capture from C 1s (with a binding energy of -540.8 eV) is explained by the fact that the occupancy number is equal to 4 in the first case and to 2 in the second one. At lower energies the relative importance of charge exchange from outer orbitals increases, depending also on the occupancy number of each one of them. It is important to note that this type of in-depth evaluation is completely impossible to obtain using Bragg's method, which however gives a general description of the reaction.

IV. CONCLUSIONS

The CDW-EIS approximation has been employed to investigate single-electron capture by fast protons impacting on small molecular targets of biological interest. The influence on total cross sections of the description of the molecular targets is analyzed. The very good agreement found between the

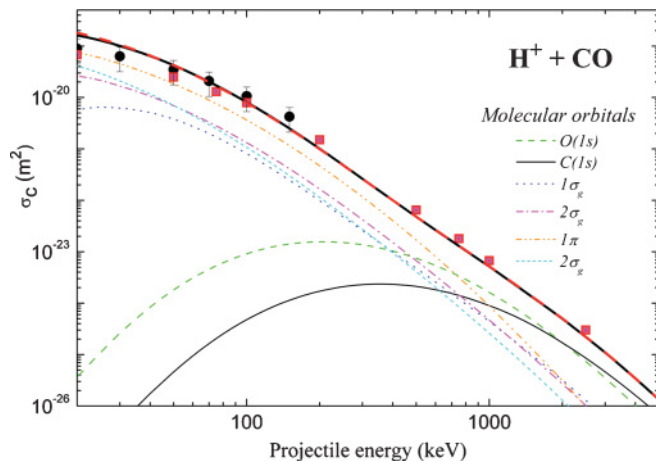


FIG. 3. (Color online) Same as Fig. 1, but for proton impact on CO.

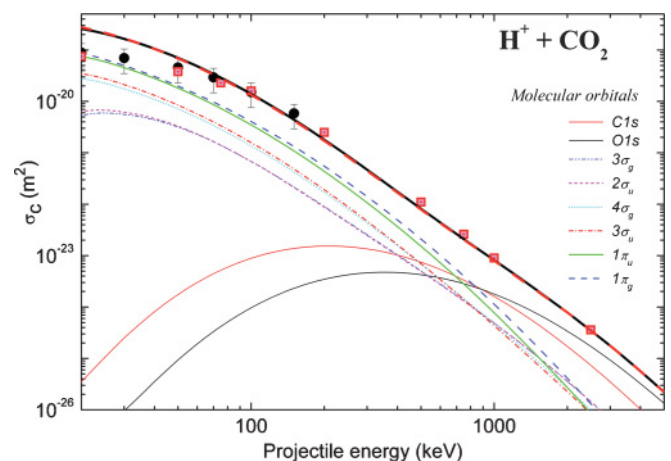


FIG. 4. (Color online) Same as Fig. 1, but for proton impact on CO_2 .

TABLE IV. Population and binding energies of the CO₂ molecular orbitals.

Molecular orbital	Population	Binding energy ε_i (eV)
O 1s	4.00 O 1s	-540.8
C 1s	2.00 C 1s	-297.5
3 σ_g	1.278 O 2s + 0.164 O 2p + 0.558 C 2s	-39.7
2 σ_u	1.306 O 2s + 0.130 O 2p + 0.564 C 2s	-37.5
4 σ_g	0.544 O 2s + 1.120 O 2p + 0.380 C 2s	-19.4
3 σ_u	0.544 O 2s + 1.120 O 2p + 0.336 C 2p	-18.1
1 π_u	2.492 O 2p + 1.508 C 2p	-17.6
1 π_g	4.00 O 2p	-13.8

theoretical total cross sections and the corresponding existing measurements reinforces the validity of the experimental findings and the recommended data. The contributions to single-electron-charge-exchange total cross sections from different

molecular orbitals are also reported. This information is of fundamental importance to feed Monte Carlo type simulations not only in biological applications but also in astrophysical ones [28,29]. The inclusion in the theoretical model of wave functions that take into account in a more precise form the molecular character of the target is a subject of our present research.

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