

Theoretical multiple-ionization cross sections of Ne-like molecules by light-ion impact: H₂OM. E. Galassi ^{1,*}, V. B. Tessaro,^{1,2} B. Gervais,³ and M. Beuve²¹*Grupo de Física Biomédica, Instituto de Física de Rosario (CONICET-UNR), Facultad de Ciencias Exactas, Ingeniería y Agrimensura, Universidad Nacional de Rosario (UNR), Rosario, Argentina*²*Université de Lyon, F-69622; Université de Lyon 1, CNRS/IN2P3, Institut de Physique Nucléaire de Lyon, Villeurbanne, France*³*Centre de Recherche sur les Ions, les Matériaux et la Photonique (UMR6252), CEA/CNRS/ENSICAEN/Université de Caen-Basse Normandie UCBN, CIMAP-CIRIL-Ganil, Boîte Postale 5133, 14070 Cedex 05, Caen, France*

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We present a simple theoretical model to calculate multiple-ionization cross sections (MICS) of Ne and Ne-like molecules (molecules with ten electrons as H₂O, CH₄, NH₃, and HF) for proton and light-ion impact, taking into account both direct and postcollisional emissions. In this paper, we tackle the case of water molecules, relevant to investigate the radiobiological effects of ion impact on living matter. The theory is developed in the framework of the independent electron model (IEM). To keep the model as simple as possible, we describe the impact parameter dependence of the single-particle ionization probabilities required by the IEM through decreasing exponential functions for each target orbital. We obtain the parameters of the exponential functions from the total net-ionization cross sections for each orbital by applying either the continuum distorted wave-eikonal initial-state (CDW-EIS) approximation or Rudd's model. We then calculate the contribution of Auger postcollisional electron emission to MICS by using the Ne postcollisional emission probabilities. This postcollisional treatment offers a very simple alternative to the much more complex molecular evaluation of postcollisional relaxation and provides results in close agreement with experimental data for proton and other light ions. We also demonstrate the relevance of considering postcollisional emission for water molecules after the 2a₁ (2s Ne-like) orbital direct ionization.

DOI: [10.1103/PhysRevA.106.012823](https://doi.org/10.1103/PhysRevA.106.012823)**I. INTRODUCTION**

Space exploration is one of the greatest human challenges. Coupled with this arises the necessity of knowing how galactic cosmic rays and secondary radiations (high-energy protons and charged nuclei) affect planetary atmospheres and astronauts' health [1]. Besides, swift ions are used in medicine in the treatment of cancer, a technique called hadrontherapy [2]. In this context, knowing how protons and heavy ions induce damage to biological tissue is a subject of current interest both from the point of view of radiation protection (thinking of the ions as carcinogenic agents) and for radiotherapy treatment planning [3]. Whereas scientific and technological knowledge has enabled us to develop many aspects of the effects of ionizing radiation, many questions remain open [4]. To understand the action of radiation in human tissues, it is necessary to refer to the initial reactions that occur when the ion goes into the cells (whose major constituent is liquid water). The first step, called the physical stage, is dominated by the ionization (single and multiple) and excitation of the molecules of the medium. After electron emission, the transient molecular ion formed in the collision dissociates [5,6], and the molecular fragments recombine to form different radicals and molecular ions (water radiolysis), such as H•, H⁺, OH, H₂O₂, HO₂, etc., [7–11]. The study of water radiolysis requires ionization

cross sections of liquid water as input for Monte Carlo simulations. Considering only single-ionization cross sections, the measured radiolytic yields cannot be reproduced; then, multiple-ionization processes must be considered. However, experimental data and theoretical models for MICS for molecular targets are scarce in the literature. From the theoretical point of view, the study of multiple electron processes is a very difficult task considering: electronic correlation, its relationship with the molecular orientation during the collision, and the projectile and residual target Coulomb potentials that could affect the emitted electrons evolution. Moreover, after the ionization of inner orbitals, a postcollisional electronic rearrangement of the target occurs, leading to electron emission. This effect plays a significant role in the molecular fragmentation during radiolysis. Such a short-time reorganization of a molecule is rather complex regarding the high degree of electronic excitation of the target when an inner electron vacancy has been created. In particular, the coupling with the numerous open channels associated with electron emission in the continuum makes the *ab initio* computation rather difficult [12–14], and alternative simpler models are highly desirable.

In previous works, direct MICS of water molecules by ion impact were added in a Monte Carlo code developed to study the physical, physicochemical, and chemical steps in water radiolysis. The direct MICS were calculated in the framework of the independent electron model (IEM) by using impact-parameter-dependent continuous distorted wave-eikonal initial state (CDW-EIS) probabilities [7]. The

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CDW-EIS probabilities were calculated by numerical integration of Bessel oscillating functions, which are very high computation time consuming. Then, in a subsequent article, the probabilities required by the IEM were modeled as exponential functions [8] to optimize the computation time. In both works, the postcollisional Auger emission (PCE) was added considering a probability equal to 1 after a direct ionization of one or two core electrons (electrons bound to the $1s$ orbital of the oxygen atom). The radiolytic yields of H_2O_2 and O_2 were in good agreement with experimental data, showing the importance of multiple-ionization processes to explain the experimental results. In more recent works, MICSs were calculated by using the nonperturbative basis generator method [14], the first Born perturbative approach [15] and the classical trajectory Monte Carlo method [16,17]. However, the contribution of Auger-like postcollisional electron emission, very important at high-energy ion impact [18], was not included in those MICS theoretical models or included considering postcollisional emission only after one $1s$ -electron removal.

The scope of the present paper is to present a simple theoretical model to calculate multiple-ionization cross sections by ion impact on Ne and the Ne-like molecules: H_2O in this article. The Ne-like molecules have the same number of electrons as Ne and have a strong monocentric character that allows us to develop a one-center “atomic” model to describe the ground-state molecular orbitals as well as the outgoing wave of the emitted electrons. The monocentric approach was applied previously to calculate single-ionization cross sections of Ne-like molecules, obtaining very good agreement with experimental data [10,19,20]. Our theoretical model for MICS calculations requires only the knowledge of the total net-ionization cross sections by each atomic or molecular orbital and the well-known Ne postcollisional emission probabilities. The proposed model can, thus, be considered as a scaled Ne model. In the next section, the theoretical model is presented, and the results are compared with experimental data and with other theoretical results. Atomic units are used hereafter except where otherwise stated.

II. THEORETICAL MODEL

The simplest way to study theoretically multielectronic transitions is using the IEM in which the interaction between the electrons is considered in a mean-field approximation. In this picture, each electron evolves independently in an effective potential created by the other electrons in their ground state. The IEM-MICS calculations require the computation of the single-particle process probabilities as a function of the impact parameter [21]. Then, we use a binomial distribution to express the probability P_q to remove q electrons from one particular shell that contains N -equivalent electrons as

$$P_q(b) = C_q^N p(b)^q [1 - p(b)]^{N-q}, \quad (1)$$

where $q = 0, 1, 2, \dots, N$ and $p(b)$ is the probability to eject an electron from the mono-electronic initial state to any mono-electronic continuum state. In this expression, $C_q^N = \frac{N!}{q!(N-q)!}$ is a binomial coefficient, and b is the impact parameter. The cross section corresponding to this multielectronic transition

reads

$$\begin{aligned} \sigma_q &= 2\pi \int_0^{+\infty} b P_q(b) db \\ &= 2\pi C_q^N \int_0^{+\infty} p(b)^q [1 - p(b)]^{N-q} db. \end{aligned} \quad (2)$$

This approximated expression for σ_q contains information both on single-electron collision and on the statistics of several equivalent electrons in the target. The cross-section σ_q is named the *exclusive* MICS [22]. The total net-ionization cross section is calculated as

$$\sigma_{\text{net}} = \sum_{q=1}^N q \sigma_q. \quad (3)$$

In the case of multielectronic targets, such as Ne and H_2O where ionization from different orbitals can occur, an extension of this formulation must be introduced. The *direct* multiple-ionization probability can be calculated as

$$P_{q,\text{dir}}(b) = \sum_{q_1, \dots, q_k=0}^{N_1, \dots, N_k} \prod_{i=1}^k \binom{N_i}{q_i} p_i^{q_i}(b) [1 - p_i(b)]^{N_i - q_i}, \quad (4)$$

where $q = q_1 + \dots + q_k$, k is the number of orbitals, $p_i(b)$ is the probability of emitting an electron from orbital i to a continuum mono-electronic state, q_i is the ionization degree of orbital i after the collision, and N_i indicates the occupation number of orbital i .

Ne and Ne-like molecules have ten bound electrons. For the first-row hydrides, the ten electrons are distributed over five orbitals with two electrons in each ($k = 5$). After ionization of internal orbitals, Auger or Coster-Kronig emission could take place. In this paper, we consider the PCE after the direct ionization of the two innermost internal orbitals of the Ne-like molecules as for the Ne atom case [18]. This approximation for the case of water molecules is supported by the similarity between the Auger spectrum for water and the Ne atoms [23,24]. This idea was applied to the carbon and oxygen atoms to study multiple ionization of CO molecules in an independent atom model, obtaining good agreement with experimental data [25]. The PCE was simulated taking into account the case of Ne but considering that C and O atoms have fewer electrons than Ne in their $2p$ subshell. However, in that work, the molecular structure (to be considered to link with the different fragmentation channels) was not taken into account because the molecule was modeled as two independent atoms at their equilibrium distance.

Following these previous ideas, but taking into account the molecular orbital structure and their binding energies, we include PCE to the MICS by adding a new factor $\mathcal{P}(q_1, q_2, \dots, q_k, \alpha)$,

$$\begin{aligned} \mathcal{P}_{q,\text{post}}(b) &= \sum_{q_1, \dots, q_k, \alpha=0}^{N_1, \dots, N_k, \alpha_{\text{max}}} \mathcal{P}(q_1, q_2, \dots, q_k, \alpha) \\ &\times \prod_{i=1}^k \binom{N_i}{q_i} p_i^{q_i}(b) [1 - p_i(b)]^{N_i - q_i}, \end{aligned} \quad (5)$$

TABLE I. Postcollisional emission probabilities after single photoionization of the $1s$ (β_1) and $2s$ (β_2) orbitals of the Ne atom [26]. The case of $\alpha = 0$ stands for luminescence, and no electron is emitted.

α	$\beta_1(\alpha)$	$\beta_2(\alpha)$
0	0.010	0.873
1	0.736	0.119
2	0.220	0.008
3	0.031	0.00
4	0.003	0.00

where α is the number of emitted electrons from the postcollisional process such that $q_1 + \dots + q_k + \alpha = q$.

In Table I, we show the experimental probabilities, $\beta_1(\alpha)$ and $\beta_2(\alpha)$ for postcollisional production of electrons if only one electron is directly removed by photoionization from the $1s$ or $2s$ orbitals of Ne, whereas all the other electrons remain bound to the target [26]. These probabilities include the postcollisional emission processes: Auger cascades (if a direct ionization of an inner shell occurs), Coster-Kronig (related to transitions into the same shell where the direct ionization occurs), and secondary contributions, such as shake-off (that accompanies sudden changes in the effective charge) and electron correlation.

Assuming that the PCE processes are independent of the primary collision, the same probabilities are considered for protons and other light ions. As we can observe, the probability of no-postcollisional emission ($\alpha = 0$) after the Ne($1s$) orbital ionization is negligibly small (0.01). Then, a very simple approximation to take into account this emission is to consider Auger-electron emission probability equal to 1 when a core electron is ionized. In that case, $\mathcal{P}(q_1 = 1, q_2, \dots, q_k, \alpha = 1) = 1$. This simplification is commonly used in Monte Carlo codes for the transport of ions and electrons in liquid water and other media [7,27,28]. In the present paper, we call this approximation 1Au.

To take into account the direct ionization of the outer electrons, and then, the lowest availability of electrons for PCE, we follow the model developed by Ref. [12] for Ne and Ar targets. Considering $k = 5$ (the case of a water molecule), the postcollisional probability is calculated as

$$\mathcal{P}(q_1, q_2, \dots, q_5, \alpha) = \sum_{\alpha_j=0}^{\alpha} \prod_{j=1}^{q_1} \mathcal{M}_1(q_2, q', \alpha_j) \prod_{j=q_1+1}^{q_1+q_2} \mathcal{M}_2(q', \alpha_j), \quad (6)$$

where $q' = q_3 + q_4 + q_5$ is the ionization degree of the three outermost orbitals in the target and $\sum_{j=1}^{q_1+q_2} \alpha_j = \alpha$. In Eq. (6), $\mathcal{M}_1(\dots, \alpha_j)$ and $\mathcal{M}_2(\dots, \alpha_j)$ are the probabilities for ejection of α_j electrons provoked by the Auger decay of one vacancy in the inner orbitals 1 or 2, respectively, accompanied by direct ionization of the outer orbitals. Then, taking into account the fact that more than one electron can be directly ionized, reducing, thus, the number of electrons that can be

TABLE II. Ne: atomic structure. In parentheses in the first column, the principal quantum number of the atomic orbital. Binding energies are in atomic units.

Atomic orbital (n_i)	Electronic population	Binding energy	
		RHF ε_i	r_i (a.u.)
$1s$ (1)	2.00 Ne $1s$	-32.77	0.1235
$2s$ (2)	2.00 Ne $2s$	-1.93	1.018
$2p$ (2)	6.00 Ne $2p$	-0.85	1.534

ejected after the collision, we set

$$\mathcal{M}_1(q_2, q', \alpha_j) = \begin{cases} 1 - \frac{8-(q_2+q')}{8} [1 - \beta_1(0)], & \alpha_j = 0, \\ \frac{8-(q_2+q')}{8} \beta_1(\alpha_j), & \alpha_j \neq 0, \end{cases} \quad (7)$$

$$\mathcal{M}_2(q', \alpha_j) = \begin{cases} 1 - \frac{6-q'}{6} [1 - \beta_2(0)], & \alpha_j = 0, \\ \frac{6-q'}{6} \beta_2(\alpha_j), & \alpha_j \neq 0. \end{cases} \quad (8)$$

A. The exponential model

To calculate MICS, single-particle-ionization probabilities $p_i(b)$ for each molecular orbital are necessary. The exponential model was used previously to calculate MICS by proton impact on Ne and Ar atoms [18] and for heavy-ion impact on He atoms [29]. In the present paper, we apply this model to light-ion impact on Ne and water molecules considered in a monocentric description. In the exponential model it is assumed that the single-particle probabilities have an exponential dependence with the impact parameter b ,

$$p_i(b) = p_i(0)e^{-b/r_i}, \quad (9)$$

where r_i is a characteristic interaction distance for each electronic orbital and $p_i(0)$ is the single-ionization probability for the zero impact parameter. In previous work, it has been observed that the CDW-EIS reduced probabilities $bp_i(b)$ for the impact of protons on Ne show the maxima at impact parameters that coincide approximately with the Hartree-Fock mean radius of the different subshells [18]. Also, the position of these maxima presents a weak dependence on the projectile energy. The reduced probability in the EM has its maximum at an impact parameter equal to r_i . Then, in the present paper, we have calculated r_i according to an extended Borh atomic model: $r_i = n_i/(-2\varepsilon_i)^{1/2}$, where ε_i is the orbital binding energy in atomic units and n_i is the principal quantum number associated with the atomic or molecular orbital. In Table II we present the parameters used for Ne. The binding energies are extracted from Roothaan-Hartree-Fock (RHF) calculations [18].

The parameter $p_i(0)$ is determined to reproduce the total net-ionization cross section per electron for each orbital σ_i/N_i . Then, after integration using expression (9) to describe the single-particle-ionization probability, we obtain that $p_i(0) = \sigma_i/2\pi N_i r_i^2$. In the present paper, we calculate the total net-ionization cross sections for each orbital using two approximations: (i) the CDW-EIS quantum-mechanical approximation for the atomic (CDW-EIS) or molecular (MO) (CDW-EIS-MO) targets as described in Ref. [30] and (ii) the semiempirical model proposed by Rudd *et al.* [31] by the

TABLE III. H_2O : molecular orbitals population and binding energies for vapor and liquid phases. In parentheses in the first column, the molecular orbital principal quantum number. Binding energies are in atomic units.

Molecular orbital (n_i)	Electronic population	Binding energy vapor	r_i vapor	Binding energy liquid	r_i liquid
$1a_1$ (1)	2.00 $\text{O}1s$	-19.84	0.1587	-19.81	0.1588
$2a_1$ (2)	1.48 $\text{O}2s$ 0.52 $\text{H}1s$	-1.184	1.299	-1.187	1.298
$1b_2$ (2)	1.18 $\text{O}2p$ 0.82 $\text{H}1s$	-0.676	1.720	-0.590	1.841
$3a_1$ (2)	0.22 $\text{O}2s$ 1.44 $\text{O}2p$ 0.34 $\text{H}1s$	-0.540	1.924	-0.492	2.016
$1b_1$ (2)	2.00 $\text{O}2p$	-0.463	2.078	-0.397	2.244

case of proton impact. In the next subsection, we present the model used to calculate the ionization cross sections with the CDW-EIS-MO approximation.

B. Molecular orbital representations and theoretical ionization cross sections

In the CDW-EIS model, the initial electron orbital wave function is distorted by a multiplicative eikonal phase associated with the projectile-electron Coulomb interaction. In the exit channel, the emitted electron is described by a double product of a plane wave and two continuum factors, associated with its interactions with the residual target (with an effective charge calculated in correspondence with the initial binding energy as $Z_{\text{eff}} = \sqrt{-2n^2\varepsilon_i}$) and with the projectile. Thus, the electron is considered to move in the combined field created by the residual target and the projectile [19]. The CDW-EIS-MO ionization cross sections for each molecular orbital are calculated by making a linear combination of atomic orbitals cross sections, whose coefficients are obtained from a population analysis [30]. This method, called complete neglect of differential overlap, allows very good agreement with the experimental differential and total-ionization cross sections for water and other small molecules. Then, it was extended to study more complex biologic molecules (as the DNA and RNA bases) with important success [32].

The model of Rudd *et al.* [31] (called Rudd here after) is a semiempirical model that allows us to calculate the single differential and total-ionization cross section for proton impact on molecular targets. Each molecular orbital is treated separately, and the cross sections are represented by analytical functions, dependent on the incident proton and the ejected electron energies. This formulation is based on the first Born approximation and uses parameters chosen to obtain the best agreement with experimental data. These cross sections are widely used, particularly, in particle transport Monte Carlo codes since their implementation is very simple.

The H_2O molecule

The electronic ground-state configuration of the water molecule in the C_{2v} symmetry group is $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$ (where the exponent gives the number of electrons per orbital). The population analysis for each orbital was performed by Senger [33] and was applied to calculate the single and multiple direct ionization cross

section for the liquid [7,8] and vapor [19] phases. We present the atomic populations and binding energies in Table III. For vapor, we use the experimental binding energies. In the case of liquid water, the binding energies are those of Dingfelder *et al.* (2000) [34].

III. RESULTS AND DISCUSSIONS

A. The Ne case

Figure 1 shows the total-net-ionization cross-sections σ_{net} for proton impact on Ne. We emphasize that σ_{net} is nothing but the cross section to emit electrons, irrespectively of the target final arrangement and is directly comparable to the electron emission recorded in an experiment. Despite some observable differences regarding the innermost orbital ionization, both CDW-EIS and the Rudd models give close agreement with experimental values. Note that we have scaled each orbital contribution by a factor of 1/10 for the sake of clarity to avoid superpositions between σ_{net} and $2p$ contributions.

In Fig. 2, we compare experimental and calculated MICSS of Ne by proton impact for single, double, and triple ionizations. The EM-CDW-EIS-post calculated using CDW-EIS and EM-Rudd-post calculated using the cross sections of Rudd *et al.* [31] show close agreement with the experimental data.

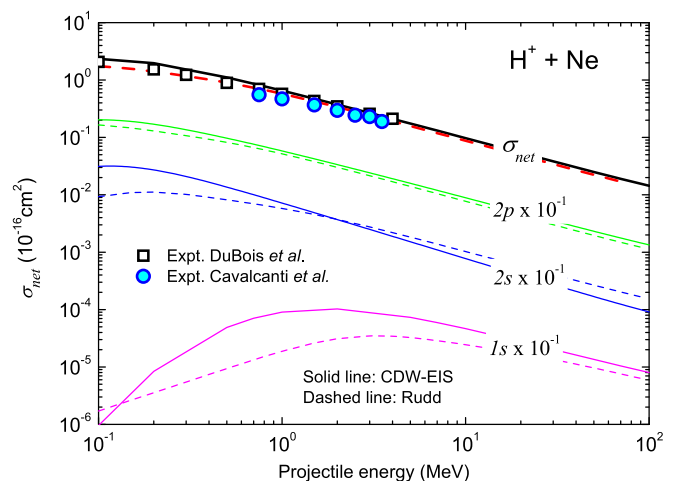


FIG. 1. Total net-ionization cross sections of Ne by proton impact. Theory: CDW-EIS: solid line; Rudd: dashed line. Experimental data: squares [35]; circles [36].

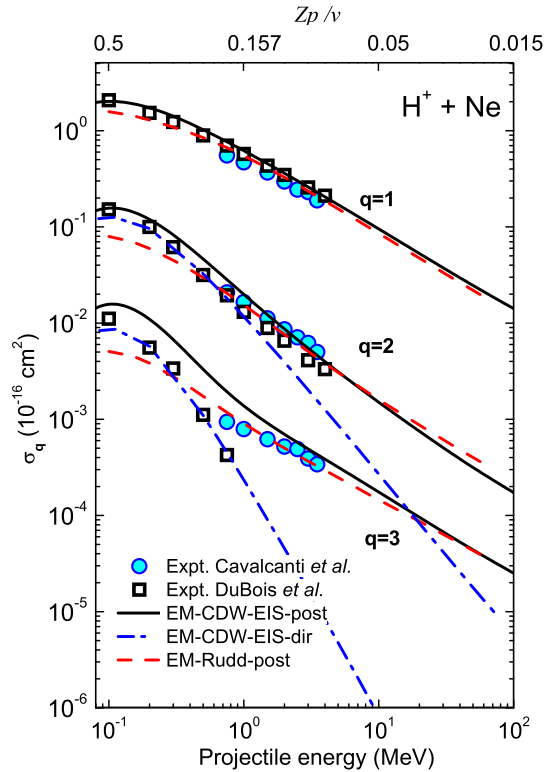


FIG. 2. Ne MICS by proton impact. Theory: EM-CDW-EIS-post: black solid line; EM-CDW-EIS-dir: blue dot-dashed line; EM-Rudd-post: red dashed line. Experimental values: blue closed circle [36]; open squares [35].

However, EM-dir (for both CDW-EIS and the Rudd models) disagrees strongly with experimental data for energies higher than 1 MeV for double and triple ionizations. This result is in agreement with the conclusions of a previous job that postulates that the Bohr parameter Z_p/v (with Z_p as the projectile charge and v as its velocity in atomic units) is appropriate to determine the region where postcollisional mechanisms begin to dominate the MICS [25]. The separation between curves corresponding to include or not PCE contributions is produced in the region where $Z_p/v \leq 0.2$ for $q = 2$ with a shift to larger values of the Bohr parameter as the ionization degree increases. For example, for 1-MeV proton impact, the Bohr parameter is 0.157, and at this energy, it is evident that EM-post and EM-dir start to separate.

We compare the ratio between multiple- and single-ionization cross sections with experimental values for Ne in Fig. 3. We include the EM-1Au results, which consider that the PCE occurs only when a core electron ($1s$ orbital) is ionized. As we can observe, this approximation gives a better agreement with experiments than EM-dir, which neglects any postcollisional effect. However, for double ionization, this approximation underestimates the experimental values by a factor of 2 for the CDW-EIS (EM-CDW-EIS-1Au) calculations and 3 for the model of Rudd (EM-Rudd-1Au). Then, the PCE associated with the ionization of the $2s$ orbital is significant for Ne. We can observe from Table I that the probability of PCE after ionization of the Ne $2s$ orbital is about 13%. Combined with the fact that the ionization cross section

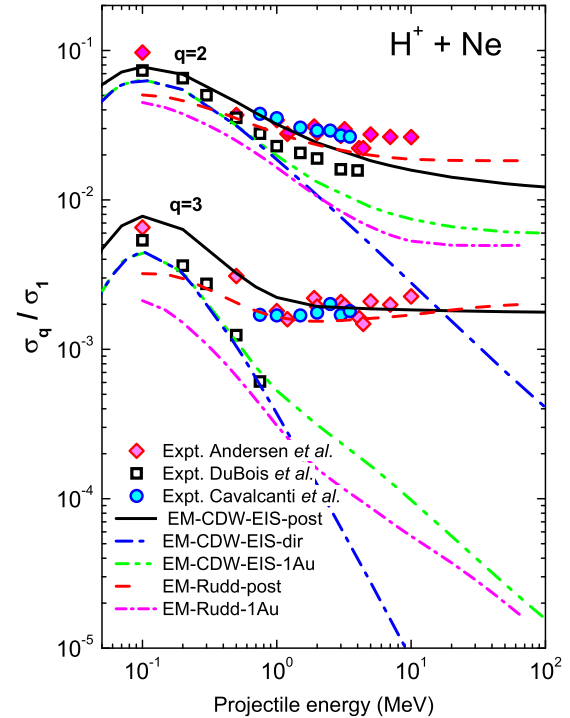


FIG. 3. Cross-section ratio (double and simple and triple and simple) for Ne by proton impact. Lines: present paper theoretical results. Experimental values: blue closed circle [36]; black open squares [35]; pink diamonds [37].

of the $2s$ orbital is much larger than the $1s$ case (typically by a factor of 10 at high energies). Then, for triple ionization, we observe that the actual contribution of the $2s$ ionization to the PCE is more important than the obtained after the $1s$ electron removal. Thus, considering only the $1s$ ionization is not sufficient to reproduce the experimental results.

In Fig. 4 we display our EM-CDW-EIS-post and EM-Rudd-post results together with that obtained by Spranger and Kirchner [12] and by Montanari *et al.* [38] and Montanari and Miraglia [39]. The former is performed for H^+ in Ne by solving numerically the time-dependent Schrödinger equation using the basis generator method (BGM) and introducing the PCE as in the present paper. The latter use the CDW-EIS approximation to calculate the single-particle probabilities required by the independent particle model with initial (bound) and final (continuum) electron wave functions expanded in products of spherical harmonics and radial wave functions, obtained through the numerical solution of the radial Schrödinger equation. For the Ne case, they consider that the Auger-like emission occurs only after K -shell ionization. We can observe that for single ionization all the models are in good agreement with experimental data. In the case of the BGM results for MICS, the theory shows good agreement with experiments for energies from 1 MeV. Discrepancies at smaller energies could be related to the use of the IEM and to the contribution of capture processes that dominates the electron loss at energies under 100 keV for proton impact [40]. The results from Montanari *et al.* [38] for double and triple ionizations underestimate the experimental data for energies where the PCE dominates the electron emission. To correct

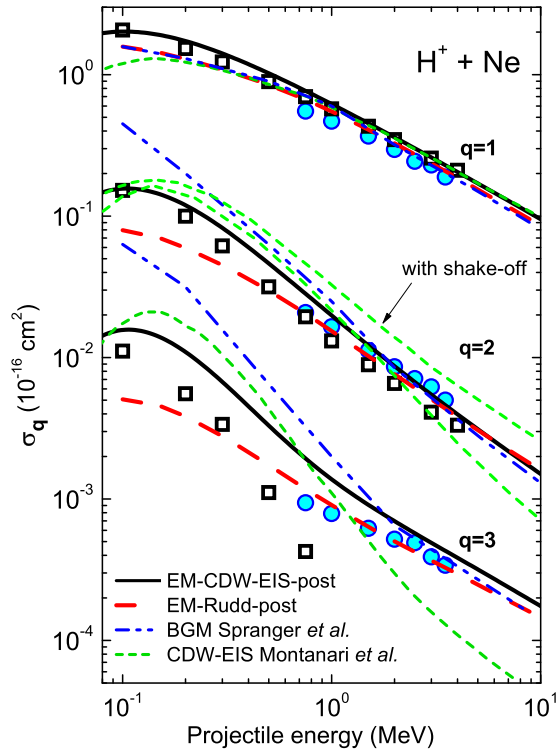


FIG. 4. Ne MICS by proton impact. Theory: EM-CDW-EIS post: black solid line; EM-Rudd-post: red dashed line; blue dot-dashed line [12]; green short-dashed line [39]. Experimental values: blue closed circle [36]; open squares [35].

this, they introduced the probability of shake-off processes to describe the postcollisional contribution for double ionization after $2s$ or $2p$ initial vacancy. This inclusion enhances all the cross sections, reproducing well the experimental trend (line indicated in the figure with an arrow). However, this treatment cannot be extended to the other ionization degrees, and the triple-ionization cross section underestimates the experimental data for energies from 1 MeV.

In Fig. 5 we show the EM-CDW-EIS-post results for He^{2+} impact on Ne as a function of ion energy, obtaining very good agreement with experimental data for $q = 1-3$. In the same figure are displayed the results from Montanari *et al.* [38] also in good agreement with experimental data in the region where direct multiple ionization dominates.

The MICS for O^{8+} (1-MeV/u) impact on Ne as a function of ionization degree q are compared with experimental values [41] in Fig. 6. As we can observe, the EM allows an excellent agreement with experimental data. In particular, in this case, the Bohr parameter is equal to 1.28 and then, no difference between the EM-CDW-EIS-dir and the EM-CDW-EIS-post is observed for ionization degrees up to $q = 5$. Clearly, the postcollisional effect is a high-velocity effect associated with inner-shell ($1s, 2s$) ionization. Another important remark is that double ionization represents $\sim 35\%$ of net ionization.

B. The H_2O case

The theoretical MICS of water by ion impact obtained applying the EM-dir and EM postapproximations are presented

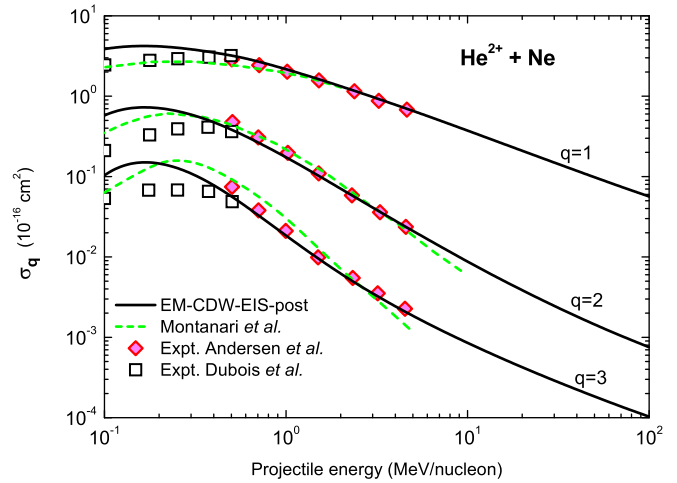


FIG. 5. Ne MICS by α -particle impact. Theory: EM-CDW-EIS-post: black solid line; green short-dashed line [38]. Experiments: black open squares [35]; pink diamonds [37].

in the next figures. The net-ionization cross sections (required by the EM) for proton impact on vapor water, calculated using the CDW-EIS-MO and the model of Rudd *et al.* [31] are displayed in Fig. 7. Both models are in good agreement with experimental data [6,42]. However, we observe that the ionization cross sections for the $1a_1$ and $2a_1$ orbitals present important differences. These differences will then affect the postcollisional contributions to MICS.

Figures 8 and 9 show MICS for proton impact on vapor water. Figure 8 shows the EM-CDW-EIS and the EM-Rudd results for $q = 1-3$ in comparison with experimental values [6]. For $q = 1$ and 2, both theoretical results considering PCE are in very good agreement with experiments. For $q = 2$, some differences between the EM-CDW-EIS-post and EM-Rudd-post appear at high energies. These differences are related to the $2a_1$ single ionization cross sections calculated within the CDW-EIS-MO and the model of Rudd *et al.* [31]

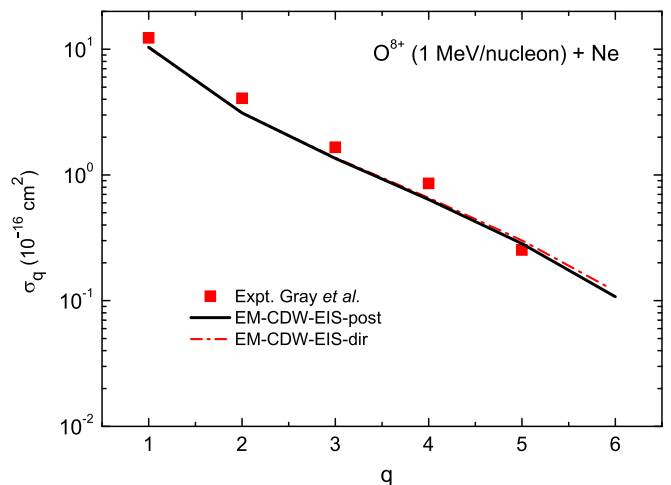


FIG. 6. Ne MICS by oxygen ion impact of 1 MeV/u as a function of ionization degree q . Theory: EM-CDW-EIS-post: black solid line; EM-CDW-EIS-dir: red dot-dashed line. Experiments: red squares [41].

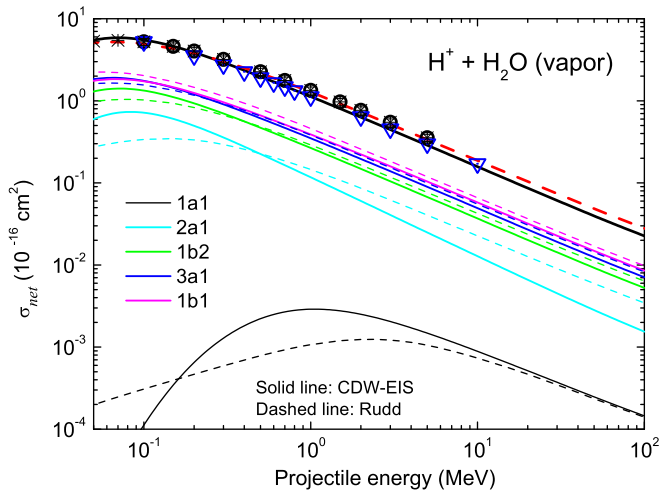


FIG. 7. Total net-ionization cross sections of H_2O by proton impact. Theoretical models: solid lines: CDW-EIS-MO; dashed lines: the model of Rudd *et al.* [31]. Experiments: open triangles [42]; stars [43]; open circles [6].

(see Fig. 7). As we can observe, EM-dir underestimates the experimental data and does not follow the same extrapolated trend.

We compare the EM with other more complex theoretical calculations for the case of proton impact in Fig. 9. The model developed by Gulyás *et al.* [44] allows the

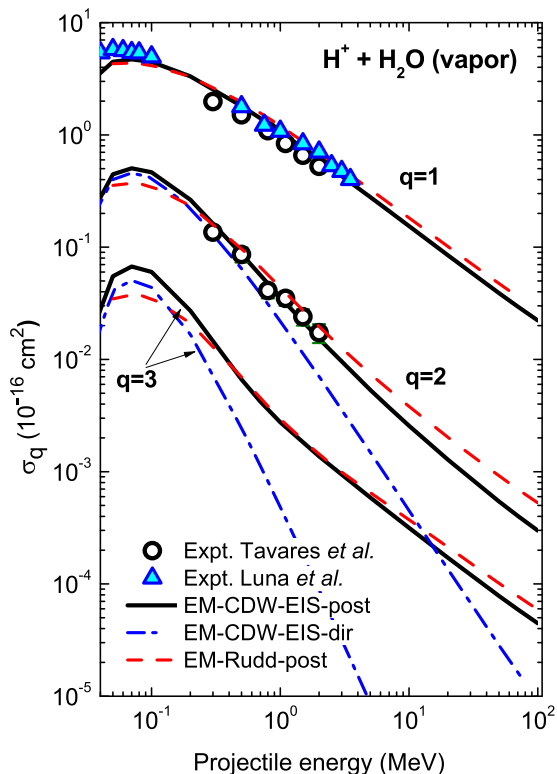


FIG. 8. H_2O MICS by proton impact. Theory: black solid line: EM-CDW-EIS-post; blue dot-dashed line: EM-CDW-EIS-dir; red dashed line: EM-Rudd-post. Experiments: open circles [6]; blue triangles: [5].

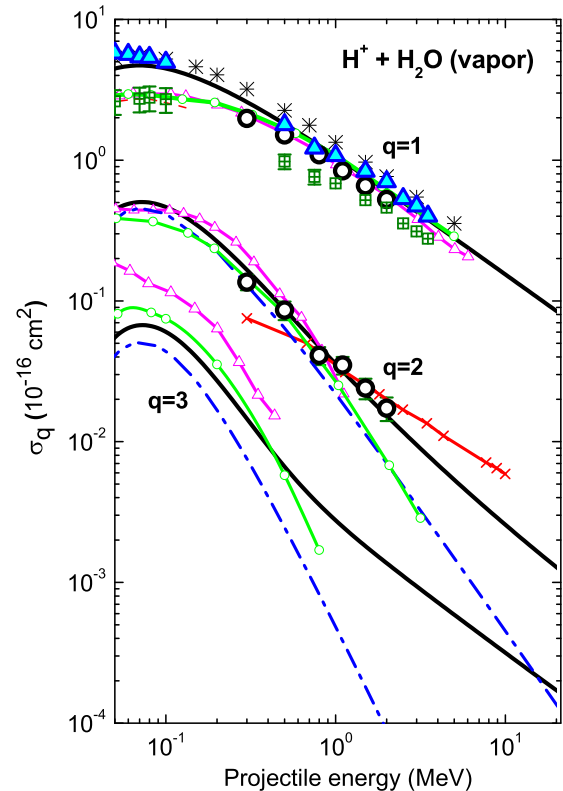


FIG. 9. H_2O MICS by proton impact. Theory: black solid line: EM-CDW-EIS-post; blue dot-dashed line: EM-CDW-EIS-dir; green circle line: [44]; pink triangle line: [14]; red cross line: [15]. Experiments: black open circles: [6]; blue triangles: [5]; stars: [43]; net-ionization cross sections: open squares [45].

calculation of direct MICS into the IEM using CDW-EIS probabilities and considering the molecular geometry configuration during the collision. This model also allows the calculation of electron capture cross sections. However, the PCE was not included. As we can observe, the results for double ionization are in good agreement with our EM-CDW-EIS-dir results. Other calculations were performed by using the nonperturbative BGM [14] to calculate charge-state correlated cross sections for single- and multiple-electron removal processes (capture and ionization) in proton- H_2O collisions. Results for $q = 1$ and 2 are in good agreement with experiments and with the theoretical EM and CDW-EIS results. However, as this model does not incorporate postcollisional emission, we expect that MICS will follow the EM-dir trend. Double-ionization cross sections calculated by using the first Born perturbative approach [15] are also included in this figure. This theoretical model involves information about the molecular geometry and the energy of the emitted electrons. The double ionization is described as a shake-off mechanism where after a single-ionization process a second electron is emitted from a relaxation process from the sudden change in the interaction potential. According to the authors, this approximation is equivalent to Auger emission. However, the direct ionization of the core electrons ($1a_1$ orbital) was not taken into account in the calculations. As we can see, the results from this method do not follow the experimental trend. Another point to highlight: the complexity

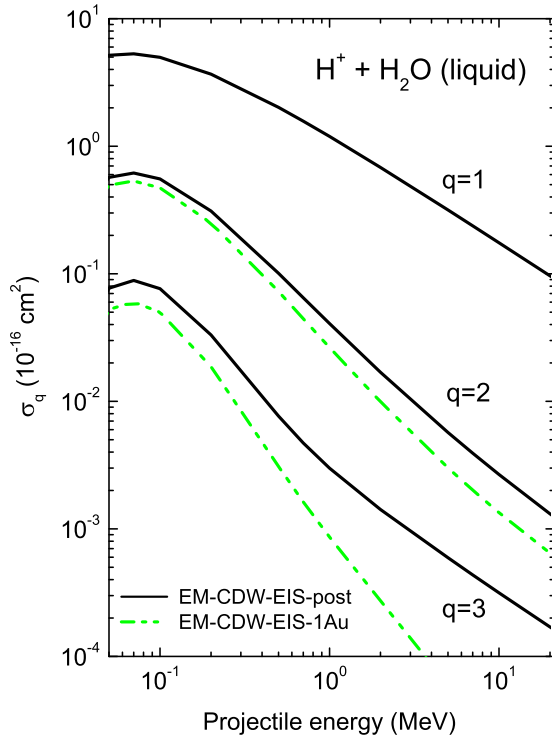


FIG. 10. Liquid-water model MICS by proton impact. Theory: black solid line: EM-CDW-EIS-post; green dot-dashed line: EM-CDW-EIS-1Au.

of this theoretical development avoids the possibility to extend the model to calculate higher multiple-ionization degrees.

In order to compare the EM-CDW-EIS-post and EM-CDW-EIS-1Au for proton impact on liquid water, we plot the results in Fig. 10. As we can observe, the EM-CDW-EIS-1Au underestimates double-ionization cross sections by a factor smaller than 2 for energies up to 100 MeV. If we do not consider PCE, the differences are higher than one order of magnitude for energies over 10 MeV. Then, considering the contribution of one postcollisional Auger emission after the $1a_1$ ionization in the Monte Carlo codes used for studying the biological effects of swift ions gives a good approximation for proton impact. In the case of higher charged ions, the PCE contribution after the $2a_1$ ionization should be considered.

Previous works showed the relevance of including MICS of water molecules in ion-track Monte Carlo codes to study the biological effects of swift ions [7,8,11,46,47]. However, as explained in the Introduction, more research was needed. In Fig. 11, double- to single-ionization cross-section ratios for proton and carbon ion impact are presented. Our EM-CDW-EIS-post results show excellent agreement with experimental values for proton impact on water vapor [6], however, EM-CDW-EIS-dir results underestimate the experimental values just as we expected. The theoretical results obtained by Champion [46] are included in this figure. In the work of Champion [46], the MICSs were obtained using a semiempirical model, based on a combination of the semiclassical statistical approximation, the statistical energy-deposition model, and the local-density approximation. To do that was introduced one adjustable parameter whose value

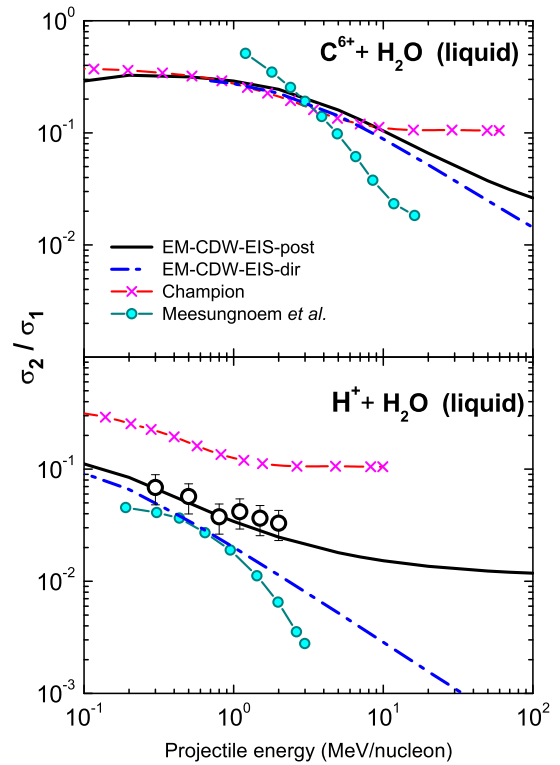


FIG. 11. Double- to single-ionization cross-section ratios for proton- and carbon-ion impacts on liquid water. Theory: black solid line: EM-CDW-EIS-post; blue dot-dashed line: EM-CDW-EIS-dir; red line with crosses: [46]; cyan line with open circles: [11]. Experiments: black open circles [6].

was obtained by extrapolating the experimental double- to single-ionization cross-section ratios for heavy-ion impact on other media, such as Ne, CO, and Ar (because were no results corresponding to water). Then, the author concluded that the double- to single-ionization cross-section ratios [in function of the projectile energy (in MeV/amu) divided by the projectile charge] is independent of the medium and the projectile ion charge. The results show good agreement with our EM-CDW-EIS-post for the case of carbon ion impact at energies up to 10 MeV/amu. However, overestimate largely the experimental data for the case of proton impact by a factor of 3.

Meesungnoem and Jay-Gerin [11] developed a particle-track Monte Carlo code to investigate the effects of multiple ionization of water molecules on the yields of formation of free radical and molecular species in the radiolysis of liquid water by ion impact. In that work, MICSs were included as adjustable parameters to reproduce experimental values of molecular oxygen radiolytic yields. The Monte Carlo also introduced other approximations (i.e., the energies of the emitted electrons after the direct multiple-ionization events were fixed) that could affect the results for radiolytic yields, contributing to the uncertainties in the MICSs obtained. The PCE was introduced as in the 1-Au approximation described before; then, the results presented by the authors correspond to direct multiple-ionization cross sections. As we can observe in Fig. 11, for proton impact the results underestimate the experimental values and our EM-CDW-EIS-dir predictions,

especially at the higher energies considered. For carbon ions, the results show a different trend in comparison with our EM-CDW-EIS-dir theoretical predictions. However, the conclusion from that work that MICS depends on the ion charge is also observed in the present paper. For the case of proton impact on liquid water, double ionization represents 1% of the ionization processes at energies higher than 1 MeV. However, when the projectile charge increases, the MICS contribution to electron emission also increases, reaching values over 20% for energies in the region of maximum dose deposition for carbon ions. Thus, a good description of these cross sections is relevant for biological effects studies.

IV. CONCLUSIONS

We presented a simple theoretical model which allows calculating in a very fast or speedway the MICS for ion impact on Ne and Ne-like molecules, in the present case H₂O. This model, developed in the independent electron model framework, use multinomial statistic with single-ionization probabilities calculated as analytical exponential functions. The exponential function's parameters are obtained from total net-ionization cross sections corresponding to each molecular or atomic orbital provided by theoretical calculations or experimental values. In the present paper, the net-ionization cross sections are calculated using the CDW-EIS and the

model of Rudd *et al.* [31], assuming a single-center character of the molecules. The multiple-ionization model includes the contribution of postcollisional Auger, Coster-Kronig, and shake-off emission to the MICS, using the measured Ne post-photoionization electron emission. The results show remarkable agreement with experimental data, despite the simplicity of our model for proton and other light ions. This paper allows us to understand the importance of considering the PCE not only after *K*-shell ionization, but also after 2*s* ionization. Its implementation in particle track Monte Carlo codes would definitely be helpful to study the damage in biological tissues induced by swift ion impact not only by that used in hadrontherapy treatments, but also for that present during long-term space travels.

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- [1] F. A. Cucinotta, K. To, and E. Cacao, Predictions of space radiation fatality risk for exploration missions, *Life Sci. Sp. Res.* **13**, 1 (2017).
 - [2] U. Amaldi, History of hadrontherapy, *Mod. Phys. Lett. A* **30**, 1 (2015).
 - [3] H. Nikjoo, S. Uehara, D. Emfietzoglou, and F. A. Cucinotta, Track-structure codes in radiation research, *Radiat. Meas.* **41**, 1052 (2006).
 - [4] L. H. Toburen, Challenges in Monte Carlo track structure modeling, *Int. J. Radiat. Biol.* **88**, 2 (2014).
 - [5] H. Luna and E. C. Montenegro, Fragmentation of Water by Heavy Ions, *Phys. Rev. Lett.* **94**, 043201 (2005).
 - [6] A. C. Tavares, H. Luna, W. Wolff, and E. C. Montenegro, Double ionization of water molecules induced by swift protons, *Phys. Rev. A* **92**, 032714 (2015).
 - [7] B. Gervais, M. Beuve, G. H. Olivera, M. E. Galassi, and R. D. Rivarola, Production of HO₂ and O₂ by multiple ionization in water radiolysis by swift carbon ions, *Chem. Phys. Lett.* **410**, 330 (2005).
 - [8] B. Gervais, M. Beuve, G. H. Olivera, and M. E. Galassi, Numerical simulation of multiple ionization and high LET effects in liquid water radiolysis, *Radiat. Phys. Chem.* **75**, 493 (2006).
 - [9] D. Boscolo, M. Krämer, M. C. Fuss, M. Durante, and E. Scifoni, Impact of target oxygenation on the chemical track evolution of ion and electron radiation, *Int. J. Mol. Sci.* **21**, 424 (2020).
 - [10] G. H. Olivera, A. E. Martinez, R. D. Rivarola, and P. D. Fainstein, Theoretical calculation of electronic stopping power of water vapor by proton impact, *Radiat. Res.* **144**, 241 (1995).
 - [11] J. Meesungnoem and J.-P. Jay-Gerin, High-LET radiolysis of liquid water with ¹H⁺, ⁴He²⁺, ¹²C⁶⁺, and ²⁰Ne⁹⁺ ions: Effects of multiple ionization, *J. Phys. Chem. A* **109**, 6406 (2005).
 - [12] T. Spranger and T. Kirchner, Auger-like processes in multiple ionization of noble gas atoms by protons, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 4159 (2004).
 - [13] A. C. K. Leung and T. Kirchner, Radiative-emission analysis in charge-exchange collisions of O⁶⁺ with argon, water, and methane, *Phys. Rev. A* **95**, 042703 (2017).
 - [14] M. Murakami, T. Kirchner, M. Horbatsch, and H. J. Lüdde, Single and multiple electron removal processes in proton-water-molecule collisions, *Phys. Rev. A* **85**, 052704 (2012).
 - [15] D. Oubaziz, R. Boulifa, Z. Aitelhadjali, and C. Champion, Double ionization of water molecules by proton impact: The role of the direct ionization mechanism, *Eur. Phys. J. D* **72**, 119 (2018).
 - [16] I. Abbas, C. Champion, B. Zarour, B. Lasri, and J. Hanssen, Single and multiple cross sections for ionizing processes of biological molecules by protons and α -particle impact: A classical Monte Carlo approach, *Phys. Med. Biol.* **53**, N41 (2008).
 - [17] N. Bachi, S. Otranto, G. S. Otero, and R. E. Olson, The role of multiple ionization of H₂O in heavy ion collisions, *Phys. Med. Biol.* **64**, 205020 (2019).
 - [18] M. E. Galassi, R. D. Rivarola, and P. D. Fainstein, Multiple electron emission from noble gases colliding with proton beams, including postcollisional effects, *Phys. Rev. A* **75**, 052708 (2007).
 - [19] R. D. Rivarola, M. E. Galassi, P. D. Fainstein, and C. Champion, Computation of distorted wave cross sections for high-energy inelastic collisions of heavy ions with water molecules, in *Advances in Quantum Chemistry. Theory of Heavy Ions Collision Physics in Hadron Therapy* (Elsevier, Amsterdam, 2013), pp. 231–263.

- [20] C. C. Montanari and J. E. Miraglia, Neonization method for stopping, mean excitation energy, straggling, and for total and differential ionization cross sections of CH₄, NH₃, H₂O, and FH by impact of heavy projectiles, *J. Phys. B: At. Mol. Opt. Phys.* **47**, 015201 (2014).
- [21] H. J. Ludde and R. M. Dreizler, Comments on inclusive cross sections, *J. Phys. B: At. Mol. Opt. Phys.* **18**, 107 (1985).
- [22] M. M. Sant'Anna, E. C. Montenegro, and J. H. McGuire, Inversion relations for exclusive and inclusive cross sections within the independent electron approximation, *Phys. Rev. A* **58**, 2148 (1998).
- [23] L. Inhester, C. F. Burmeister, G. Groenhof, and H. Grubmüller, Auger spectrum of a water molecule after single and double core ionization, *J. Chem. Phys.* **136**, 144304 (2012).
- [24] P. Kolorenč and V. Averbukh, K-shell auger lifetime variation in doubly ionized ne and first row hydrides, *J. Chem. Phys.* **135**, 134314 (2011).
- [25] C. A. Tachino, M. E. Galassi, and R. D. Rivarola, Role of Auger-type emission from diatomic molecular targets interacting with fast multicharged ions, *Phys. Rev. A* **80**, 014701 (2009).
- [26] A. T. Carlson, E. W. Hunt, and O. K. Manfred, Relative abundances of ions formed as the result of inner-shell vacancies in atoms, *Phys. Rev.* **151**, 41 (1966).
- [27] M. Dingfelder, R. H. Ritchie, J. E. Turner, W. Friedland, H. G. Paretzke, and R. N. Hamm, Comparisons of calculations with PARTRAC and NOREC: Transport of electrons in liquid water, *Radiat. Res.* **169**, 584 (2008).
- [28] S. Incerti *et al.*, Geant4-DNA example applications for track structure simulations in liquid water: A report from the Geant4-DNA project, *Med. Phys.* **45**, e722 (2018).
- [29] M. E. Galassi, R. D. Rivarola, and P. D. Fainstein, A simple method to evaluate double ionization of he by swift highly charged ions, *Nucl. Instrum. Methods Phys. Res. Sect. B* **268**, 1637 (2010).
- [30] M. E. Galassi, R. D. Rivarola, M. Beuve, G. H. Olivera, and P. D. Fainstein, Theoretical calculation of single ionization in collisions between protons and low-[Formula Presented] molecules at intermediate and high energies, *Phys. Rev. A* **62**, 022701 (2000).
- [31] M. E. Rudd, Y.-K. Kim, D. H. Madison, and T. J. Gay, Electron production in proton collisions with atoms and molecules: Energy distributions, *Rev. Mod. Phys.* **64**, 441 (1992).
- [32] M. E. Galassi, C. Champion, P. F. Weck, R. D. Rivarola, O. Fojón, and J. Hanssen, Quantum-mechanical predictions of DNA and RNA ionization by energetic proton beams, *Phys. Med. Biol.* **57**, 2081 (2012).
- [33] B. Senger, Calculated molecular double-differential cross-sections for ionisation under proton impact, *Eur. Phys. J. D* **9**, 79 (1988).
- [34] M. Dingfelder, M. Inokuti, and H. G. Paretzke, Inelastic-collision cross sections of liquid water for interactions of energetic protons, *Radiat. Phys. Chem.* **59**, 255 (2000).
- [35] R. D. DuBois, L. H. Toburen, and M. E. Rudd, Multiple ionization of rare gases by H and He, *Phys. Rev. A* **29**, 70 (1984).
- [36] E. G. Cavalcanti, G. M. Sigaud, E. C. Montenegro, M. M. Sant'Anna, and H. Schmidt-Böcking, Post-collisional effects in multiple ionization of neon by protons, *J. Phys. B: At. Mol. Opt. Phys.* **35**, 3937 (2002).
- [37] L. H. Andersen, P. Hvelplund, H. Knudsen, S. P. Moller, A. H. Sorensen, K. Elsener, K.-G. Rensfelt, and E. Uggerhoj, Multiple ionization of He, Ne, and ar by fast protons and antiprotons, *Phys. Rev. A* **36**, 3612 (1987).
- [38] C. C. Montanari, J. E. Miraglia, W. Wolff, H. Luna, A. C. F. Santos, and E. C. Montenegro, Multiple ionization of atoms including post-collisional contributions, *J. Phys.: Conf. Ser.* **388**, 012036 (2012).
- [39] C. C. Montanari and J. E. Miraglia, Antiproton, proton and electron impact multiple ionization of rare gases, *J. Phys. B: At. Mol. Opt. Phys.* **45**, 105201 (2012).
- [40] T. Kirchner, H. J. Ludde, and R. M. Dreizler, Effective single-particle description of single and multiple processes in P + Ne collisions, *Phys. Rev. A* **61**, 012705 (1999).
- [41] T. J. Gray, C. L. Cocke, and E. Justiniano, Charge-state correlated cross sections for the production of low-velocity highly charged Ne ions by heavy-ion bombardment, *Phys. Rev. A* **22**, 849 (1980).
- [42] W. E. Wilson, J. H. Miller, L. H. Toburen, and S. T. Manson, Differential cross sections for ionization of methane, ammonia, and water vapor by high velocity ions, *J. Chem. Phys.* **80**, 5631 (1984).
- [43] M. E. Rudd, T. V. Goffe, R. D. DuBois, and L. H. Toburen, Cross sections for ionization of water vapor by 7–4000-keV protons, *Phys. Rev. A* **31**, 492 (1985).
- [44] L. Gulyás, S. Egri, H. Ghavamnia, and A. Igarashi, Single and multiple electron removal and fragmentation in collisions of protons with water molecules, *Phys. Rev. A* **93**, 032704 (2016).
- [45] H. Luna, A. L. F. de Barros, J. A. Wyer, S. W. J. Scully, J. Lecoindre, P. M. Y. Garcia, G. M. Sigaud, A. C. F. Santos, V. Senthil, M. B. Shah, C. J. Latimer, and E. C. Montenegro, Water-molecule dissociation by proton and hydrogen impact, *Phys. Rev. A* **75**, 042711 (2007).
- [46] C. Champion, Multiple ionization of water by heavy ions: A monte carlo approach, *Nucl. Instrum. Methods Phys. Res. Sect. B* **205**, 671 (2003).
- [47] G. H. Olivera, C. Caraby, P. Jardin, A. Cassimi, L. Adoui, and B. Gervais, Multiple ionization in the earlier stages of water radiolysis, *Phys. Med. Biol.* **43**, 2347 (1998).