Scaling rules for the ionization of biological molecules by highly charged ions

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We investigate scaling rules for the ionization cross sections of multicharged ions on molecules of biological interest. The cross sections are obtained using a methodology presented in [Mendez *et al.* J. Phys B (2020)], which considers distorted-wave calculations for atomic targets combined with a molecular stoichiometric model. We examine ions with nuclear charges Z from +1 to +8 impacting on five nucleobases –adenine, cytosine, guanine, thymine, uracil–, tetrahydrofuran, pyrimidine, and water. We investigate ~~the scaling~~ scaling rules of the ionization cross section with the ion charge and the number of active electrons per molecule. Combining these two features, we define a scaling law ~~independent of the ion charge and the complexity of the molecular target~~ for any ion and molecular target , which is valid in the intermediate to high energy range~~. Then~~, i.e., 0.2-5 MeV/amu for oxygen impact. Thus, the forty ion-molecule systems analyzed here can be merged into a single band. We confirm the generality of our independent scaling law with several collisional systems.

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I. INTRODUCTION

The interest in the ionization of biological molecules by multicharged ions has increased due to medical and environmental implementations [1], including medical treatments [2–4] and contaminant recognition in biological materials [5, 6]. Many semiempirical [7] and theoretical efforts are currently being undertaken [8–13] to get reliable values for the ionization cross sections of these molecular systems.

In recent work [8], we combined the continuum distorted-wave calculations (CDW) for atoms and the simple stoichiometric model (SSM) to approximate the ionization cross sections of complex molecular targets by the impact of charged ions. The molecular ionization cross section σ_M was expressed as a linear combination of atomic CDW calculations σ_A, weighted with the number of atoms for each specie n_A, i.e, $\sigma_M = \sum_A n_A \sigma_A$. The CDW-SSM approximation showed consistent results for over a hundred of biologically relevant ion-molecule systems. As expected, in the high energy range (i.e., above 5 MeV/amu), the ionization cross sections of the molecular systems follow the Z^2 dependence predicted by the first Born approximation. However, at intermediate energies, the dependence with Z is not straightforward since non-perturbative models are mandatory.

This contribution constitutes a follow-up ~~to~~ of our previous work [8]. We introduce here a two-folded scaling rule for the ionization cross sections of complex molecules by charged ions. Our approach considers the dependence of the cross section with the ion charge Z and incorporates the scaling of the ionization with the number of active electron n_e of the molecular targets. Scaling rules are generally very useful since they can be used as first-order approximations in experimental measurements and multipurpose codes.

II. SCALING RULES

A. Scale with the ion charge

In the development of our scaling rule, we examine forty collisional systems. The target-ion systems are composed of eight targets: the DNA and RNA nucleobases –adenine, cytosine, guanine, thymine, uracil–, tetrahydrofuran (THF), pyrimidine, and water; and five ion species: H^+, He^{+2}, Be^{+4}, C^{+6}, and O^{+8}. We consider these systems as a benchmark for the present rule.

We found two types of Z-scaling laws in the literature applicable to the intermediate impact energy range. The rule suggested by Janev and Presnyakov [14] ~~depends linearly with ion charge Z, considering~~ considers σ/Z versus E/Z to be the *natural* reduced form of the ionization cross section σ and the incident ion energy E. More recently, Montenegro and co-workers [15, 16] suggested an alternative scaling by taking into account that the cross section is a function of Z^2/E at high energies. Their scaling, given by

$$\sigma/Z^{\alpha} = f(E/Z^{2-\alpha}), \tag{1}$$

keeps the Z^2/E relationship for any value of the parameter α. The authors proposed $\alpha = 4/3$ for the ionization of He and H_2 by differently charged ions [15].

Following the work of Montenegro and collaborators, we found that the parameter that best converges the CDW-SSM cross sections of the forty collisional systems over the broadest energy range is $\alpha = 1.2$. The validity of this particular scaling is evident in Fig. 1, where –for each target– the CDW-SSM curves corresponding to different ions lay one over the other. It is worth noting that our theoretical results are valid for impact energies above the maximum of the cross sections, which corresponds to an impact energy range from 50 keV for H^+ to 250 keV/amu for O^{+8}.

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FIG. 1. (Color online) Scaled ionization cross section σ/Z^{α} as a function of ion impact energy $E/Z^{2-\alpha}$ with $\alpha = 1.2$. Colors are associated with the incident ion labeled on top of the figure. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of ○ H^{+} [18] and ◊ C^{+6} [21] on adenine; H^{+} on △ uracil [17], ⊖ C^{+4}, ⊕ C^{+6}, O^{+6}, F^{+6}, and ⊗ O^{+8}, F^{+8} on uracil [22, 23]; H^{+} on ▽ pyrimidine [19], and ◇ THF [20]; ⊙ [24], ⊛ [25], Ⓐ [26], ⊘ [27] H^{+}, ⊜ [28], ⊜ [29], ⊘ [27] He^{+2}, Ⓥ C^{+6} [31, 32], and ⃠ O^{+8} [33] on water. Markers □ [34], ▷ [35], ◁ [36], and ☆ [37] correspond to electron impact ionization with the equi-velocity conversion.

We also examined the experimental data available for the forty ion-target systems [17–33] with the Z^{α}-scaling rule. For targets with none or little experimental data, we included electron impact ionization results [34–37] at high velocity with the corresponding equivelocity conversion. As can be noted, most of the data in Fig. 1 confirm the present scaling, even for O^{+8} in water [33]. Only two data sets are off our predictions: the ionization ~~data~~ cross sections of uracil by swift C, O, and F ions from Refs~~. [22, 23]are too low compared with our CDW-SSM results, and the data~~ [22, 23]; and the values for Li^{+3} in water from Ref. [30] ~~spread out from the present theoretical curves~~ for $E < 600$ keV/amu. ~~For targets with none or little experimental data, we included electron impact ionization results [34–37] at high velocity with the corresponding equivelocity conversion~~In the case of uracil, recent CTMC calculations by Sarkadi [38] are also above the experimental values by Tribedi group [22, 23].

B. Scale with the molecular target

The good results obtained in the scaling with the ion charge encouraged us to further investigate a scaling law that could predict values for ionization cross sections of any ion in any molecule. To this end, we considered the number of active electrons in each molecule n_e proposed in Ref. [8] and combined it with the Z^α-scaling from Section II A.

In our previous work, we noticed that the CDW ionization cross ~~section~~ sections, σ_A ~~of~~ , of atomic targets H, C, N, ~~O targets~~ and O scale with the number of active electrons per atom ν_A, as $\sigma_e = \sigma_A/\nu_A$, where ν_A is 1 for H and 4 for C, N, ~~and~~ O, i.e.,

$$\frac{\sigma_{\mathrm{H}}}{1} \sim \frac{\sigma_{\mathrm{C}}}{4} \sim \frac{\sigma_{\mathrm{N}}}{4} \sim \frac{\sigma_{\mathrm{O}}}{4} \,. \qquad (2)$$

By ~~considering~~ means of the SSM, we define the number of active electrons per molecule as $n_e = \sum_A n_A \nu_A$. The n_e values for the molecular targets considered ~~throughout~~ throughtout this work are displayed in Table I. The scaling with the molecular number of active electrons proved to give excellent results, as shown in Fig. 6 of Ref. [8].

C. Scale with the ion charge and the molecular target

By incorporating the Z^α reduction and the ~~molecular~~ scaling with the number of active ~~electron scaling~~electrons, we introduce the scaled and reduced ionization cross section of molecules $\tilde{\sigma}$, which is expressed as a function of $E/Z^{2-\alpha}$, and it is given by

$$\tilde{\sigma} = \frac{\sigma_e}{Z^\alpha} = \frac{\sigma_M/n_e}{Z^\alpha} \,, \qquad (3)$$

where σ_M is the ionization cross section for the molecular target, n_e is the number of active electrons per molecule displayed in Table I ~~,~~ and the parameter is $\alpha = 1.2$. Fig. 2 shows the ~~reduced-scaled~~ theoretical and experimental ~~data from Fig. 1 obtained using~~ values of $\tilde{\sigma}$ (given by Eq. (3)) for all the systems displayed in Fig. 1. As can be noted, the scaling works very well and is independent of the ion charge or the complexity of the molecular target. Our theoretical curves lay in a narrow band valid for any charged ion (reduced with Z^α) in any molecule (scaled with the number of active electrons) with a dispersion of about 20%. If we consider the experimental data, the uncertainty of our scaling grows to 30%, which is ~~shown with~~ coverd by the gray area in Fig. 2. It is worth noting that we did not include in ~~Fig. 1~~ this figure the data for uracil from Refs. [22, 23], and for Li^{+3} on water [30]. The discussion about these experimental values exceeds the present work.

We consider ~~our scaling law~~ this scaling robust enough to be valid for different ~~ion-molecule~~ ion–molecule combinations. We tested the generality of our model by including in Fig. ~~1~~ 2 several data sets of molecular targets

Molecule	n_e	Molecule	n_e	Molecule	n_e
H_2O	6	CO_2	12	$C_4H_5N_3O$	37
N_2	8	C_4H_8O	28	$C_5H_6N_2O_2$	42
O_2	8	$C_4H_4N_2$	28	$C_5H_5N_5$	45
CH_4	8	$C_4H_4N_2O_2$	36	$C_5H_5N_5O$	49

TABLE I. Number of active electrons per target at intermediate to high energies obtained from the CDW calculations [8].

not considered previously, such as the measurements by Rudd *et al.* [29, 39] for H^+ and He^{+2} in N_2, O_2, CH_4, CO and CO_2, and the ~~most recent data~~ recent values by Luna *et al.* [40] for H^+ in CH_4~~by Luna *et al.* [40]~~.

The good agreement shown in Fig. 2 ~~summarizes~~ summaries the main result of this work, and holds the validity of the present scaling ~~with the ion charge and the number of active electrons in the target.~~ for different ions and targets. Although the theoretical CDW-SSM results are valid for energies above the maximum of the cross sections, ~~it is worth noting from Fig. 2 that~~ the scaling of the experimental data extends even to lower impact energies, as can be noted in Fig. 2. New measurements for other ions and molecules are expected to reinforce the present proposal.

III. CONCLUSIONS

We present scaling rules for the ionization cross sections of highly charged ions in biological targets. The first scaling reduces the nature of the projectile by scaling the cross section with the ion charge, Z^α, as a function of the reduced impact energy $E/Z^{2-\alpha}$, with $\alpha = 1.2$. The second scaling considers the molecular ~~characteristics~~ characteristic of the target by taking into account the number of active electrons per molecule, n_e. The last scaling law combines the Z^α-reduction with the n_e-scaling of ~~the~~ cross section, ~~becoming~~ and it becomes independent of the ion charge and the molecular target. The scalings are obtained by means of CDW-SSM calculations for five different charged ions in eight targets and tested with the available experimental data. The generality of our independent scaling is proved to be valid in a wide energy range by considering a significant number of experimental data sets for other collisional systems.

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FIG. 2. (Color online) Ionization cross section reduced with the ion charge Z and scaled with number of active electrons per molecule n_e, given by Eq. (3) with $\alpha = 1.2$. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of H^+ on ○ adenine [18], △ uracil [17], ▽ pyrimidine [19] and ◇ THF [20]; ◊ C^{+6} on adenine [21]; ⊙ [24], ⊛ [25], ⊘ [26], ⊘ [27] H^+, ⊜ [28], ⊜ [29], ⊘ [27] He^{+2}, ⊚ C^{+6} [31, 32], and ⃠ O^{+8} [33] on water. H^+ impact on ⊞ N_2, ⧈ O_2, ◫ CO, ⧅ CO_2, and ⊡ CH_4; and He^{+2} impact on ⊞ N_2, ⧈ O_2, ◫ CO, ⧅ CO_2, and ⊡ CH_4 [29, 39], ⊘ H^+ on CH_4 [40]; and electron impact on ▷ pyrimidine [35], and ◁, ☆ [36, 37] THF.

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