~~Universal~~ General scaling rule for the ionization of biological molecules by highly charged ions

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(Dated:)

In the present work, we investigate scaling rules for the ionization cross sections of multicharged ions on molecules of biological interest. The cross sections are obtained ~~from distorted wave calculations for atomic targets combined with a stoichiometric model for the molecules proposed~~ 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 ~~in~~ impacting on five nucleobases –adenine, cytosine, guanine, thymine, uracil–, tetrahydrofuran, pyrimidine, and ~~also in~~ water. We propose a scaling with the ion charge, which is valid in the intermediate to high energy range, i.e., 0.2-5 MeV/amu for oxygen impact. We extend our work to a universal scaling for any ion and molecule, merging the forty ~~ion molecule~~ ion-molecule systems analyzed here into a single band. Furthermore, our model proved to be valid for other molecules too.

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

~~Recently~~ In recent work [8], we combined the ~~continue distorted-wave~~ continuum distorted-wave calculations (CDW) for atoms and the simple stoichiometric model (SSM), also known as the Bragg sum rule, to approximate the ionization cross sections of complex molecular targets by charged ions ~~[8]. The CDW-SSM approximation showed reasonable~~. The CDW-SSM approximation showed consistent results for over a hundred of ~~ion molecule~~ ion-molecule systems. As expected, in the high energy range (i.e., above 5 MeV/amu), the ionization cross sections ~~present~~ of the molecular systems follow the Z^2 dependence predicted by the first Born approximation. However, at intermediate energies, the dependence with Z is ~~more complex, and non-perturvative~~ not straightforward since non-perturbative models are mandatory.

~~The intention of this letter is~~ This letter intends to give a follow up of our previous work ~~[8]~~ by proposing a scaling ~~with the ion charge Z of~~ rule for the ionization cross sections of complex molecules ~~,~~ with the ion charge Z, which is valid at intermediate energies. In general, scaling rules are used as ~~first-order tests~~ first-order approximations in experimental measurements and multipurpose codes. ~~Based on [8], we propose a universal scaling for any ion-target system~~ Furthermore, we explore the generality of our scaling rule by inspecting various other ion-target systems.

~~At intermediate impact energies,~~ We have found in the literature two scaling rules applicable at intermediate impact energy range. The scaling rule suggested by Janev and Presnyakov [14] ~~suggest~~ depends linearly with ion charge Z, considering σ/Z versus E/Z ~~as~~ to be the *natural* reduced form of the ionization cross section σ and the incident ion energy E. ~~Much more~~ More recently, Montenegro and ~~co-workers [15, 16]~~ co-workers [15, 16] proposed an alternative scaling by taking into account that ~~σ~~ the cross section is a function of Z^2/E. 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. In Ref. [15], the authors propose $\alpha = 4/3$ for ionization of He and H_2 by ~~different~~ differently charged ions.

~~(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.~~

Combining our recent ~~CDW-SSM~~ CDW-SSM results [8] and Eq. (1), we propose here a Z-scaling and implement it for forty collisional systems. The ~~ion molecule~~ ion-molecule systems are composed of eight targets: the DNA and RNA nucleobases –adenine, cytosine, guanine, thymine, uracil–, tetrahydrofuran (THF), pyrimidine, and water; and five ~~charged ions~~ ion species: H^+,

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].

He^{+2}, Be^{+4}, C^{+6}, and O^{+8}. We considered these systems as a benchmark for the present scaling.

We found that the parameter α from Eq. (1) that fits the CDW-SSM scaled cross sections for all the ions is $\alpha = 1.2$. The validity of the theoretical scaling with the ion charge is evident in Fig. 1, where the CDW-SSM curves lay one over the other. Our theoretical results are valid for impact energies around and 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}.

The scaling was tested with the experimental data available for ionization by the impact of differently charged ions [17–25, 29–31, 33], and also by electron impact at sufficiently high velocity [34–37]. As can be noted, most of the data in Fig. 1 confirm the present scaling, even for O^{+8} in water [33]. However, the data of uracil by swift C, O, and F ions in [22, 23] are too low compared with our CDW-SSM results, but also as compared with Itoh et $al.$ data [17], and with the CTMC calculations by Sarkadi [38]. The data for Li^{+3} in water from Ref. [30] also spreads out from the present theoretical curves for $E < 600$ keV/amu.

The good results obtained in the scaling with the ion charge challenged us to look for a more general scaling rule that could predict values for ionization cross sections of any ion in any molecule. To that end, we resorted to the number of active electrons in each atom n_e proposed in [8], and combined it with the Z-scaling displayed in Fig. 1.

The CDW ionization cross sections σ^{CDW} of atomic H, C, N, O targets scale as $\sigma_e = \sigma^{CDW}/n_e$ with n_e being 1 for H, 4 for C, N, and O, i.e.,

$$\frac{\sigma_H^{CDW}}{1} \sim \frac{\sigma_C^{CDW}}{4} \sim \frac{\sigma_N^{CDW}}{4} \sim \frac{\sigma_O^{CDW}}{4} \qquad (2)$$

The SSM leads to the molecular numbers of active electrons included in Table I.

The universal scaling we propose here is expressed as σ_U as a function of $E/Z^{2-\alpha}$, with

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

σ is the ionization cross section for the molecular target, $\alpha = 1.2$ and n_e is the number of active electrons per molecule given in Table I. In Fig. 2, we test the universal scaling of Eq. (3) for all the theoretical and experimental values displayed in Fig. 1. We also included a gray area representing the 30% deviation of our theoretical curves. As can be noted, the universal scaling works very well. All the curves and data lays in a narrow band valid for any charged ion (scaled with Z) in any molecule (scaled with the number of active electrons). We decided not to include in 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.

In principle, the $universal$ scaling should be valid for different ion–molecule combinations. We proved this statement by including in Fig. 2 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 recent values by Luna et $al.$ [40] for H^+ in CH_4.

The good agreement shown in Fig. 2 summaries the main result of this work, and holds the validity of our universal scaling. Although the theoretical CDW-SSM results are valid for energies above the maximum of the cross sections, the scaling of the experimental data extends to lower impact energies, as can be noted in Fig. 2. The importance of scaling rules lays in their predictive capability. New measurements for other ions and molecules are expected to reinforce the present proposal.

I. CONCLUSIONS

In this letter, we present a scaling for the ionization cross sections of highly charged ions in biological targets. The scaling rule states the cross sections divided by Z^α as a function of the reduced impact energy $E/Z^{2-\alpha}$, with $\alpha = 1.2$. The scaling was obtained by means of the CDW-SSM calculations for five different charged ions in eight targets and tested with the available experimental data. A universal scaling rule is also proposed, which reduced the cross sections with the number of active electrons of the molecule. The universal scaling proved to be valid for a large number of experimental data.

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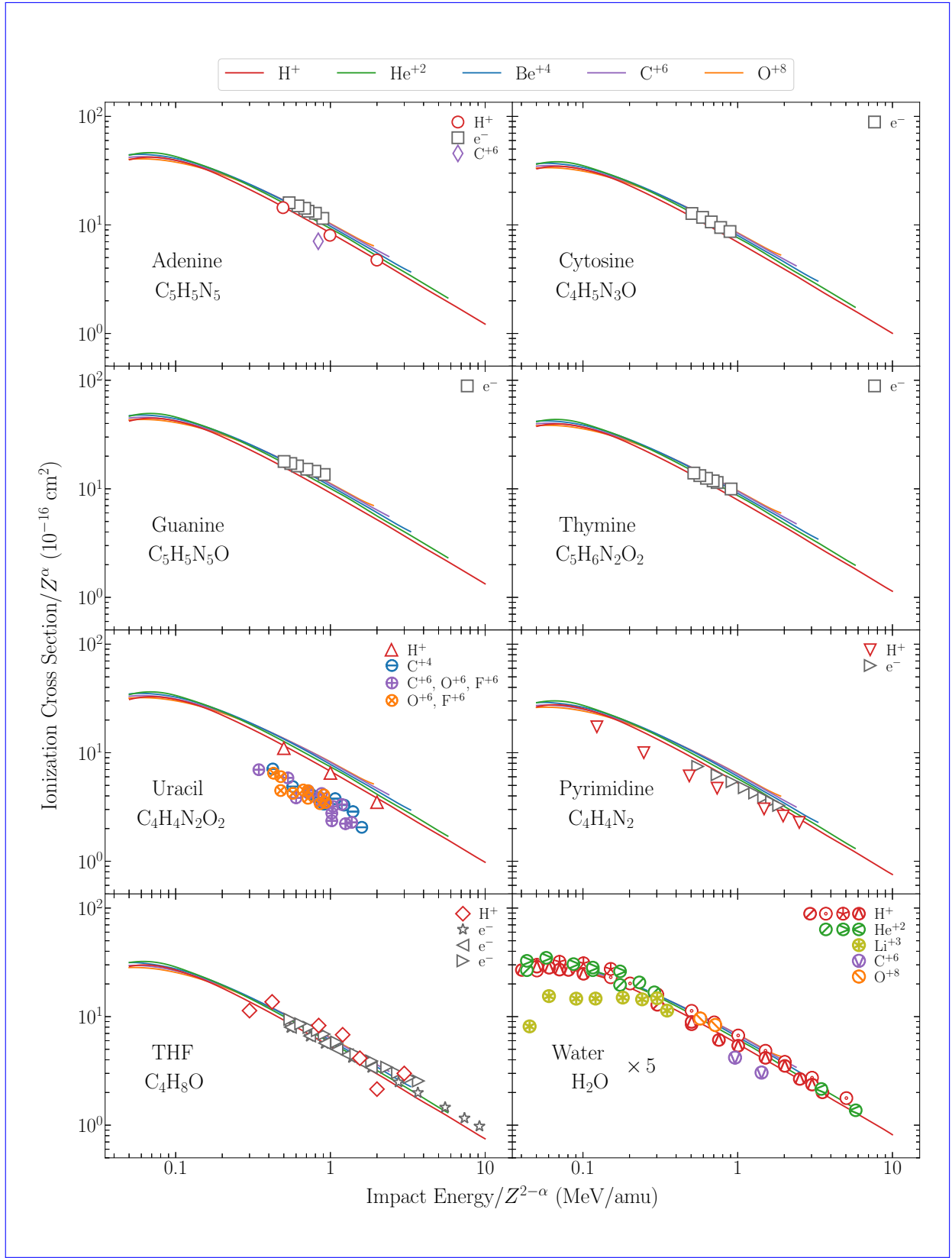[40] H. Luna, W. Wolff, and E. C. Montenegro, L. Sigaud, Phys. Rev. A **99**, 012709 (2019).

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.
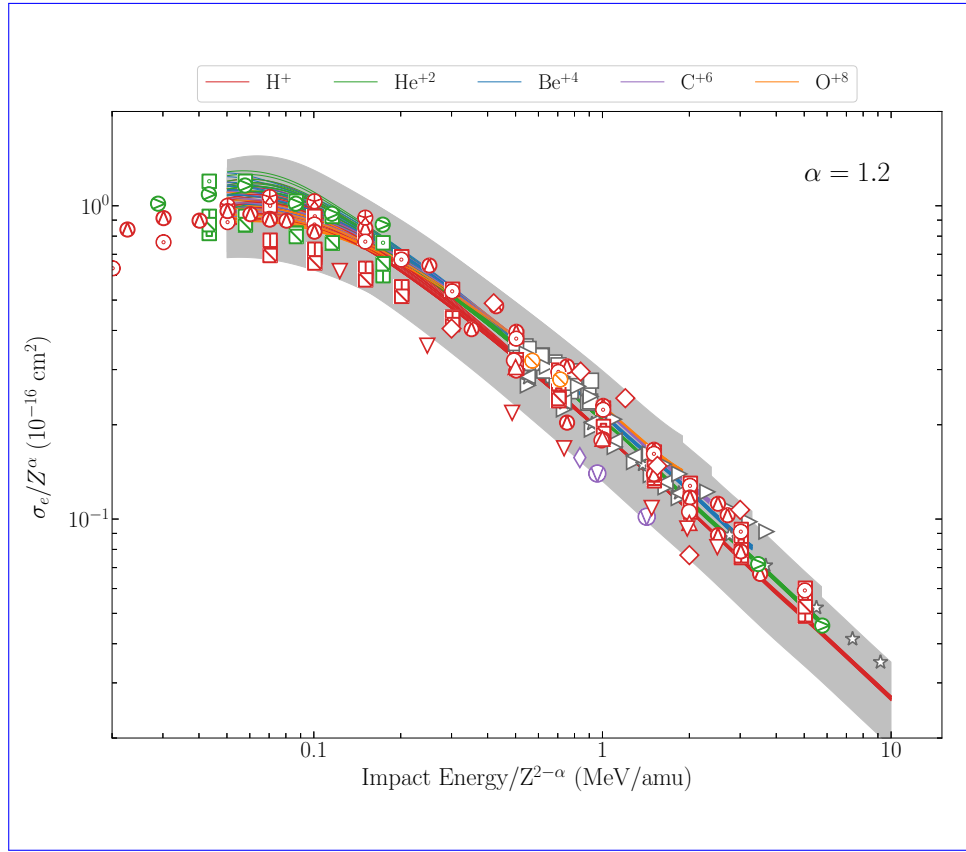
FIG. 2. (Color online) Universal scaling with the ions charge Z and the number of active electrons in the molecule n_e given by Eq. (3) with $\alpha = 1.2$. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of H^+ on ◯ adenine [18], △ uracil [17], ▽ pyrimidine [19] and ◇ THF [20]; ◇ 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.