Universal scaling 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 in [Mendez *et al.* J. Phys B (2020)]. We examine ions with charges Z from +1 to +8 in 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 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 [1], from medical treatments [2–4] to 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 molecules.

Recently, we combined the continue distorted–wave calculations (CDW) for atoms and the simple stoichiometric model (SSM) to approximate the ionization cross sections of complex molecular targets by charged ions [8]. The CDW–SSM approximation showed reasonable results for over a hundred of ion–molecule systems. As expected, in the high energy range (i.e. above 5 MeV/amu) the ionization cross sections present the Z^2 dependence predicted by the first Born approximation. However, at intermediate energies, the dependence with Z is more complex, and non–perturvative models are mandatory.

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

At intermediate impact energies, Janev and Presnyakov [14] suggest σ/Z versus E/Z as the *natural* reduced form of the ionization cross section σ and the incident ion energy E. Much more recently, Montenegro and co–workers [15, 16] proposed an alternative scaling by taking into account that σ is a function of Z^2/E. Their scaling, given by

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

keeps the Z^2/E relationship for any value of α. In Ref. [15], the authors propose $\alpha = 4/3$ for ionization of He and H_2 by different charged ions.

Combining our recent CDW–SSM results [8] and Eq. (1), we propose here a Z-scaling and implement it

for forty collisional systems. The ion–molecule systems are composed of eight targets: the DNA and RNA nucleobases –adenine, ~~citosine~~cytosine, guanine, thymine, uracil–, tetrahydrofuran (THF), pyrimidine, and water; and five charged ions: H^+, 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 very clear in Fig. 1, where the CDW-SSM curves lays one over the other. Our theoretical results are valid for impact energies around and above the maximum of the cross sections, which means above 50 keV for impact of H^+ to 250 keV/amu for impact of O^{+8}.

The scaling was tested with the experimental data available by impact of different charged ions [17–29], and also by electron impact at sufficiently high velocity [30–33]. As can be noted, most of the data in Fig. 1 confirms the present scaling, even for O^{+8} in water [29]. 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 [34]. The data for Li^{+3} in water from Ref. [27] 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 $\sigma_e = \sigma^{\text{CDW}}/n_e$ with n_e being 1 for H, 4 for C, N, and O. The SSM leads to the molecular numbers of active electrons included in Table I.
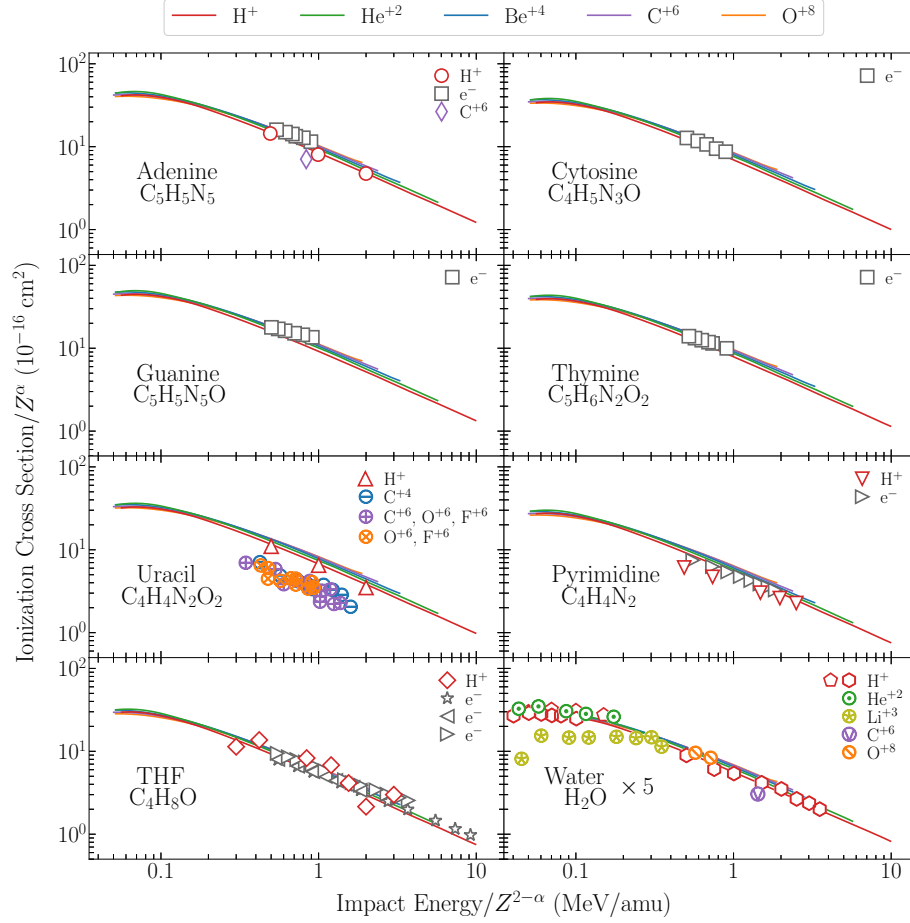
FIG. 1: (Color online) Scaled ionization cross section σ/Z^α as a function of ion impact energy $E/Z^{2-\alpha}$. Colors are associated with the incident ion labeled on top of the figure. Curves: present CDW–SSM theoretical results. Symbols: experimental impact of ○ H^+ [18] and ◊ C^{+6} [21] on adenine; 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]; ○ H^+ [24], ⌢ H^+ [25], ⊙ He^{+2} [26], ⊛ Li^{+3} [27], Ⓥ C^{+6} [28], and ⊘ O^{+8} [29] on water. Markers □ [30], ▷ [31], ◁ [32], and ☆ [33] correspond to electron impact ionization with the equi-velocity conversion.

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].

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

$$\sigma_U = \frac{\sigma_e}{Z^\alpha} = \frac{\sigma/n_e}{Z^\alpha}, \qquad (2)$$

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. (2) for all the theoretical and experimental values displayed in Fig. 1. As can be noted, the universal scaling works well, all the curves and data lays in a narrow band valid for any charged ion (scaling with Z) in any molecule (scaling with the number of active electrons). We decided not including in this figure the data for uracil from Ref. [22, 23], and for Li^{+3} on water Ref. [27]. 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.* [26, 35] for H^+ and He^{+2} in N_2, O_2, CH_4, CO and CO_2, and the recent values by Luna *et al.* [36] 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 ex-
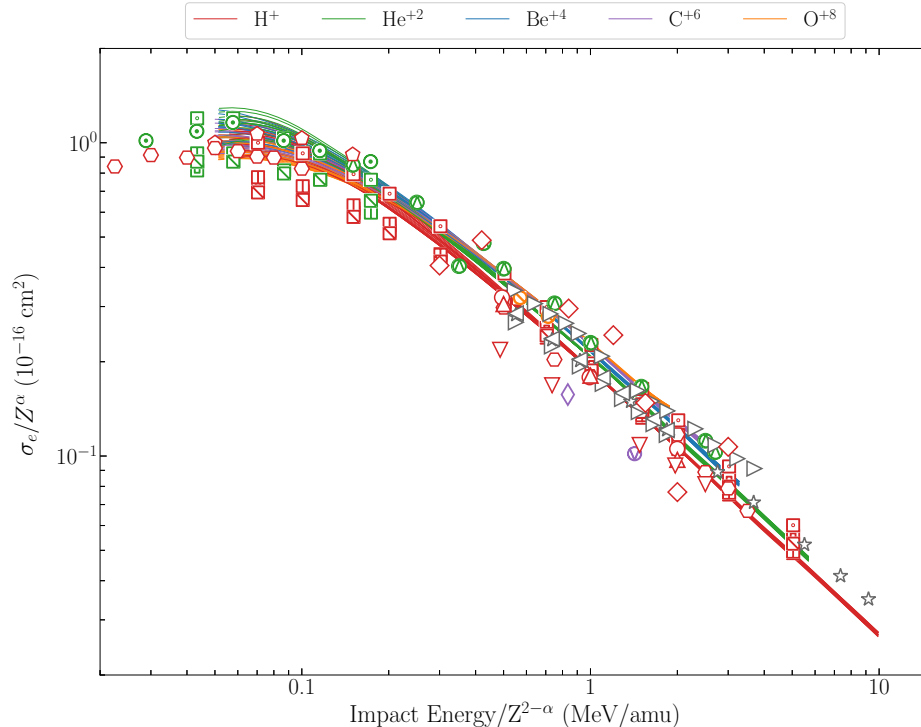
FIG. 2: (Color online) Universal scaling with the ions charge Z and the number of active electrons in the molecule n_e given by Eq. (2). Curves: present CDW-SSM theoretical results. Symbols: experimental impact of H^+ on ○ adenine [18], △ uracil [17], ▽ pyrimidine [19] and ◇ THF [20]; ◊ C^{+6} on adenine [21]; ◯ H^+ [24], ◠ H^+ [25], ⊙ He^{+2} [26], Ⓥ C^{+6} [28], and ⊠ O^{+8} [29] on water; H^+ and He^{+2} impact on ⊞ N_2, ⊡ O_2, ⊞ CO, ⊠ CO_2, and ⊡ CH_4 [26, 35], ⊘ H^+ on CH_4 [36]; and electron impact on ▷ pyrimidine [31], and ◁, ☆ [32, 33] THF.

tends to lower impact energies, as can be noted in Fig. 2. The importance of scaling rules ~~lay on~~ 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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