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

A. M. P. Mendez, C. C. Montanari, J. E. Miraglia
Instituto de Astronomía y Física del Espacio (CONICET–UBA), Buenos Aires, Argentina.
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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 ~~the pyrimide bases: adenine~~five nucleobases –adenine, citosine, guanine, thymine, ~~uracil~~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 ~~oxigen~~ oxygen impact. We extend ~~it~~ our work to a universal scaling for any ion and molecule, ~~which merges~~ merging the forty ion–molecule systems analyzed here ~~in~~ into a single band~~, and~~. Furthermore, our model proved to be valid for other molecules too.

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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 recognition of contaminants~~ [2–4] to contaminant recognition in biological materials [5, 6]. Many semiempirical [7] and theoretical efforts are currently being ~~done~~ 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]. This CDW-SSM~~ [8], The CDW–SSM approximation showed reasonable results for ~~six ions in seventeen molecules~~over a hundred of ion–molecule systems. As expected, in the high energy range (i.e. above 5 MeV/amu) the ionization cross sections ~~have~~ present the Z^2 dependence predicted by the first Born approximation. ~~Instead~~However, at intermediate energies, the dependence with Z is more complex, and ~~non-perturvative~~ non–perturvative models are mandatory.

The ~~aim~~ intention of this letter is to ~~deep on~~ give a follow up of our previous work~~in~~ [8] by proposing a scaling with the ion charge Z of the ionization cross sections of complex molecules~~with the ion charge Z~~, valid at intermediate energies. ~~The requirements of values for a multiplicity of systems make this kind of scalings very interesting as a first order test for new~~ In general, scaling rules are used as first–order tests in experimental measurements and ~~as inputs in~~ multipurpose codes. Based on ~~the scaling of the ionization cross sections with the number of active electrons~~ [8], we propose ~~an~~ a universal scaling for any ~~ion-target system, valid at least for the complex biological molecules studied here.~~

ion–target system.

At intermediate impact energies, ~~the Z^2 rule no longer holds.~~ 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~~ co–workers [15, 16] proposed an alternative scaling by taking into account that σ is a function of Z^2/E~~, so an scaling~~. Their scaling, given by

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

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

Combining ~~Eq.~~ our recent CDW–SSM results [8] and Eq. (1)~~and our recent CDW-SSM results [8]~~, we propose here a Z-scaling and ~~tested it for eight targets (~~implement it for forty collisional systems. The ion–molecule systems are composed of eight targets: the DNA and RNA ~~nucleo-basis: adenine, cytosine~~nucleobases –adenine, citosine, guanine, thymine, ~~uracil, also~~ uracil–, tetrahydrofuran (THF), pyrimidine, and water~~)~~; and five charged ions~~(~~: H^+~~m~~, He^{+2}, Be^{+4}, C^{+6}, and O^{+8}~~)~~. We considered these ~~forty collisional systems as~~ systems as a benchmark for the present scaling.

We found that ~~σ/Z^{α} vs.$E^{2-\alpha}$, with $\alpha = 1.2$ best fits the CDW-SSM~~ 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 ~~figure~~ Fig. 1, where the CDW-SSM curves lays one over the other. ~~Out~~ 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 ~~figure 1 verifies the scaling quite well. The~~ 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 ~~as~~

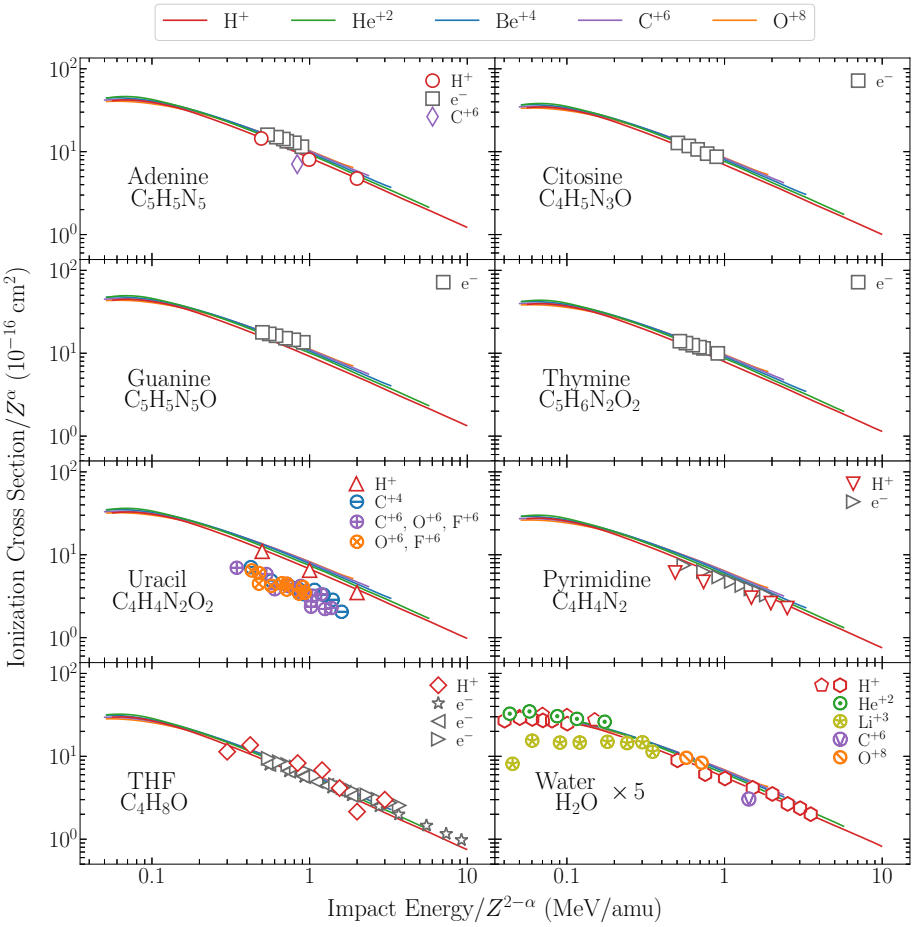

FIG. 1: (Color online) Scaled ionization cross section σ/Z^α as a function of ion impact energy $E/Z^{2-\alpha}$ ~~as explained in Eq. (1)~~.Colors are ~~asociated~~ associated with the ~~impact charge as signed in the upper part~~ incident ion labeled on top of the figure. Curves: present ~~CDW-SSM~~ 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.

compared with our ~~CDW-SSM~~ 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 ~~in [27] also separate~~ 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 ~~figure~~ Fig. 1.

The CDW ionization cross sections ~~σ^{CDW}~~ $\sigma^{\rm CDW}$ of atomic H, C, N, O targets scale as ~~$\sigma_e = \sigma^{CDW}/n_e$~~ $\sigma_e = \sigma^{\rm CDW}/n_e$ 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~~ Table I.

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

$$\sigma_U = \frac{\sigma_e}{Z^\alpha} = \frac{\sigma/n_e}{Z^\alpha} ,$$

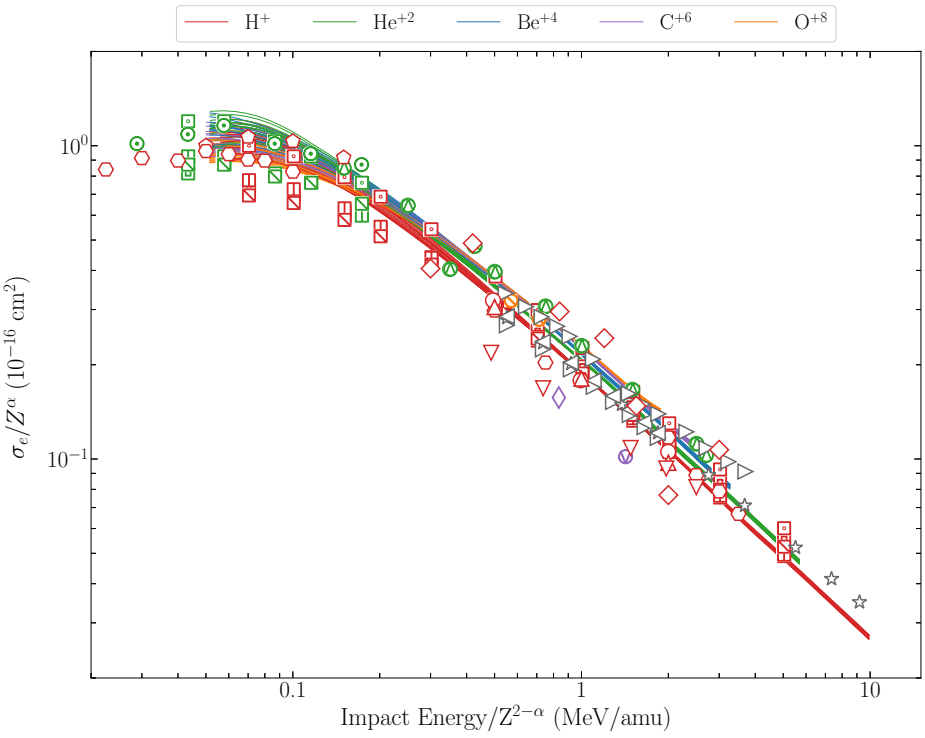

FIG. 2: (Color online) Universal scaling with the ions charge Z and the number of active electrons in the molecule n_e given by Eq. (2). Curves: present CDW-SSM theoretical results. Symbols: experimental impact of H^+ on ○ adenine [18], △ uracil [17], ▽ pyrimidine [19] and ◇ THF [20]; ◊ C^{+6} on adenine [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.

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 ~~being~~ is the ionization cross section for the molecular target, α = 1.2 and n_e ~~being~~ is the number of active electrons per molecule ~~in table~~ given in Table I. In ~~figure~~ ~~2~~Fig. 2, we test the universal scaling of Eq. (2) for all the theoretical and experimental values displayed in ~~figure~~ Fig. 1. As can be noted, the universal scaling works ~~fine~~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 ~~in~~ from Ref. [22, 23], and for Li~~on water in~~ $^{+3}$ 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~~ ion–molecule combinations. We proved this statement by including in ~~figure~~ Fig. 2 the measurements by Rudd ~~et al~~ *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~~ *et al.* [36] for H^+ in CH_4.

The good agreement shown in ~~figure 2 resumes~~ Fig. 2 summaries the main result of this work, and holds the validity of ~~present~~ our universal scaling. Although the theoretical ~~CDW-SSM~~ 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 ~~figure~~ Fig. 2. The importance of scaling rules lay on ~~the~~ their predictive capability. New measurements for other ions and molecules are expected to reinforce the present proposal.

I. CONCLUSIONS

In this letter, we present ~~an~~ 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 α = 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. ~~An~~ A universal scaling rule is also proposed, which reduced the cross sections with the number of active elec-

trons of the molecule. The universal scaling proved to be valid for a large number of experimental data.

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