~~Universal scaling~~

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

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(Dated:)

~~In the present work, we~~ 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~~ Furthermore, we introduce a modified scaling rule, which takes into account the number of active electrons per molecule. This scaling rule is independent of the ion charge and the nature of the molecular target, and it allows us to merge the forty ion-molecule systems analyzed here into a single band. ~~Furthermore, our model proved to be valid for other molecules too~~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 ~~gained increasing interest~~ increased due to medical and environmental ~~reasons~~implementations [1], ~~from~~ including medical treatments ~~[2–4] to~~ [2–4] 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 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 ~~ion–molecule~~ biologically relevant 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 to give a follow up~~ This contribution constitutes a follow-up of our previous work ~~[8] by proposing a scaling~~. 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 ~~cross sections of complex molecules, valid at intermediate energies. In general, scaling rules are used as first–order tests~~ with the number of active electron n_e of the molecular targets. Scaling rules are in generally very useful since they can be used as first-order approximations in experimental measurements and multipurpose codes. ~~Based on [8], we propose a universal scaling for any ion–target system.~~

~~At intermediate impact energies,~~

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

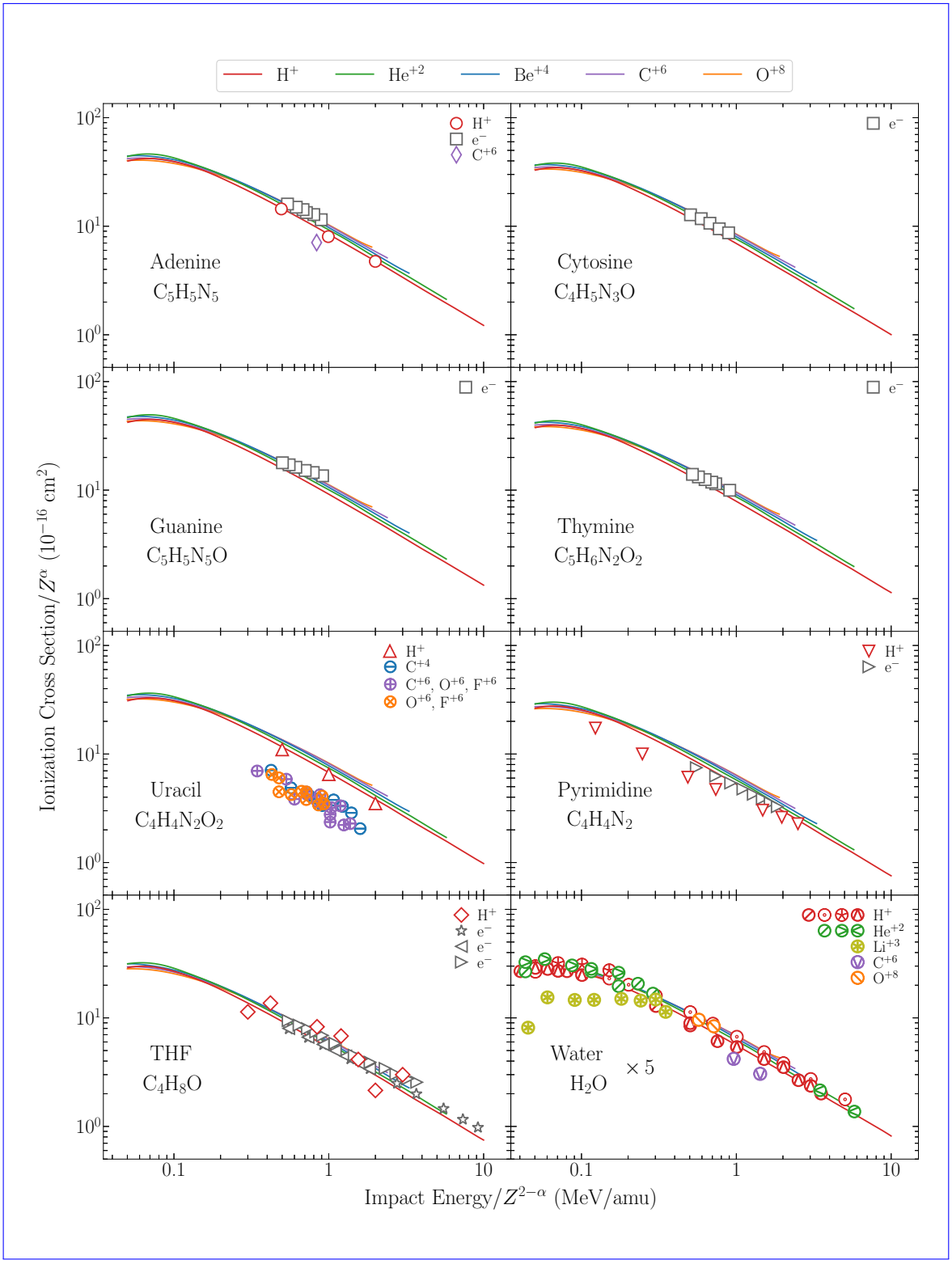

FIG. 1. (Color online) Scaled ionization cross section σ/Z^α as a function of ion impact energy $E/Z^{2-\alpha}$ with $\alpha = 1.2$. Colors are associated with the incident ion labeled on top of the figure. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of ○ H^+ [18] and ◊ 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.

rule suggested by Janev and Presnyakov [14] ~~suggest~~ depends linearly with ion charge Z, considering σ/Z ver-

sus 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] proposed~~ co-workers [15, 16] suggested an alternative scaling by taking into account that ~~σ~~ the cross section is a function of Z^2/E at high energies. Their scaling, given by

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

keeps the Z^2/E relationship for any value of the parameter α. ~~In Ref. [15], the authors propose~~ The authors proposed $\alpha = 4/3$ for the ionization of He and H_2 by ~~different 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 results [8] and Eq. (??), 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, 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.~~ differently charged ions [15].

~~We~~ Following the work of Montenegro and collaborators, we found that the parameter ~~α from Eq. (??) that fits the CDW-SSM scaled cross sections for all the ions~~ 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 ~~the theoretical scaling with the ion charge is very clear~~ this particular scaling is evident in Fig. 1, where ~~–for each target–~~ the CDW-SSM curves ~~lays~~ corresponding to different ions lay one over the other. ~~Our~~ It is worth noting that our theoretical results are valid for impact energies ~~around and~~ above the maximum of the cross sections, which ~~means above~~ corresponds to an impact energy range from 50 keV for ~~impact of~~ H^+ to 250 keV/amu for ~~impact of~~ O^{+8}.

~~The scaling was tested with~~ We also examined the experimental data available ~~by impact of different charged ions [17–25, 29–31, 33], and also by electron impact at sufficiently high velocity [34–37]~~ for the forty ion-target systems [17–33] with the Z^{α}-scaling rule. As can be noted, most of the data in Fig. 1 ~~confirms~~ confirm the present scaling, even for O^{+8} in water [33]. ~~However,~~ ~~the~~ Only two data sets are off our predictions: the ionization data of uracil by swift C, O, and F ions ~~in~~ from Refs. [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~~ CDW-SSM results, and the data for Li^{+3} in water from Ref. [30] ~~also spreads~~ 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.

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].

B. Scale with the molecular target

The good results obtained in the scaling with the ion charge ~~challenged us to look for a more general scaling rule~~ encouraged us to further investigate a scaling law that could predict values for ionization cross sections of any ion in any molecule. To ~~that~~ this end, we ~~resorted to~~ considered the number of active electrons in each ~~atom~~ molecule n_e proposed in ~~[8],~~ Ref. [8] and combined it with the ~~Z~~Z^{α}-scaling ~~displayed in Fig. 1~~ from Section II A.

~~The CDW ionization cross sections $\sigma^{\rm CDW}$ of atomic~~ In our previous work, we noticed that the CDW atomic ionization cross section σ_A of H, C, N, O targets scale ~~as $\sigma_e = \sigma^{\rm CDW}/n_e$ with n_e being~~ with the number of active electron per atom ν_A, where ν_A is 1 for H ~~,~~ and 4 for C, N, and O~~, i. e.~~

$$\frac{\sigma_{\rm H}^{\rm CDW}}{1} \sim \frac{\sigma_{\rm C}^{\rm CDW}}{4} \sim \frac{\sigma_{\rm N}^{\rm CDW}}{4} \sim \frac{\sigma_{\rm O}^{\rm CDW}}{4}$$

~~The SSM leads to the molecular numbers~~. By considering the SSM, we define the number of active electrons ~~included in Table I~~ per molecule $n_e = \sum_A n_A \nu_A$, which are given in Table I for the molecular targets considered throughtout this work. The scaling with the molecular number of active electrons (see Fig. 6 of Ref. [8]) gave excellent results and proved to be a good scaling.

~~(Color online) Universal scaling with the ions charge Z and the number of active electrons in the molecule n_e given by Eq. (??). 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.~~

C. Scale with the ion charge and the molecular target

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

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

~~σ~~ where σ_M 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~~ I and the parameter is $\alpha = 1.2$. Fig. 2 ~~, we test the universal scaling of Eq. (??) for all the~~ shows the reduced-scaled theoretical and experimental ~~values displayed in Fig.1. We also included a gray area representing the 30% deviation of our theoretical curves~~data from Fig. 1 obtained using Eq. (2). As can be noted, the ~~universal~~ scaling works very well ~~. All the curves and data lays~~ 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 (~~scaled with Z~~reduced with Z^α) in any molecule (scaled with the number of active electrons) ~~.~~ ~~We decided not to include in this figure~~ with a dispersion of about xx%. If we consider the experimental data, the uncertainty of our scaling grows to 30%, which is shown with the gray area. It is worth noting that we did not include 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~~

We consider this scaling robust enough to be valid for different ion–molecule combinations. We ~~proved this statement by including~~ tested the generality of our scaling by including several data sets of molecular targets that were not considered previously. We included 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~~ 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. The importance of scaling rules lays in their predictive capability.~~ . New measurements for other ions and molecules are expected to reinforce the present proposal.

III. CONCLUSIONS

~~In this letter, we present a scaling~~

We present scaling rules for the ionization cross sections of highly charged ions in biological targets. The ~~scaling rule states the cross sections divided by~~ 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 ~~scaling was~~ second scaling considers the molecular characteristic of the target by taking into account the number of active electrons per molecule, n_e. The last scaling law combines the Z-reduction with the n_e-scaling of cross section, and it becomes independent of the ion charge and the molecular target. The scalings were 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~~ The generality of our independent scaling is proved to be valid ~~for a large~~ in a wide energy range by considering a significant number of experimental data ~~.~~ sets for other collisional systems.

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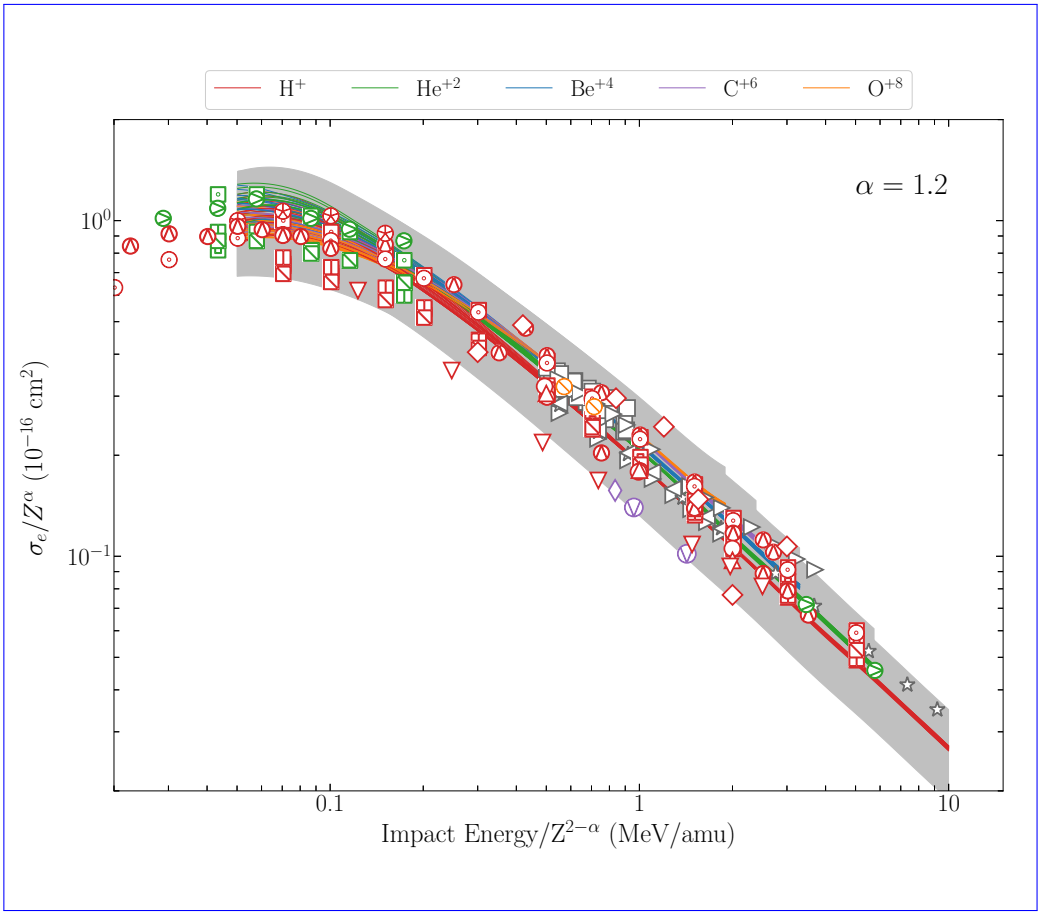

FIG. 2. (Color online) Universal scaling with the ions charge Z and the number of active electrons in the molecule n_e given by Eq. (2) with $\alpha = 1.2$. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of H^+ on ○ adenine [18], △ uracil [17], ▽ pyrimidine [19] and ◇ THF [20];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