General scaling rule 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.
(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 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 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.

PACS numbers: 34.50Gb, 34.80Gs, 34.80Dp
Keywords: ionization, scaling, molecules, charged-ions, DNA, multicharged ions

The ionization of biological molecules by multicharged ions has gained increasing interest due to medical and environmental implementations [1], which includes 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), also known as the Bragg sum rule, to approximate the ionization cross sections of complex molecular targets by charged ions. The CDW-SSM approximation showed consistent 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 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 letter intends to give a follow up of our previous work by proposing a scaling 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 approximations in experimental measurements and multipurpose codes. Furthermore, we explore the generality of our scaling rule by inspecting various other ion-target systems.

We have found in the literature two scaling rules applicable at intermediate impact energy range. The scaling rule suggested by Janev and Presnyakov [14] depends linearly with ion charge Z, considering 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] proposed an alternative scaling by taking into account that 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 differently 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, cytosine, guanine, thymine, uracil–, tetrahydrofuran (THF), pyrimidine, and water; and five ion species: 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 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

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].

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

$$\frac{\sigma_{\rm H}^{\rm CDW}}{1} \sim \frac{\sigma_{\rm C}^{\rm CDW}}{4} \sim \frac{\sigma_{\rm N}^{\rm CDW}}{4} \sim \frac{\sigma_{\rm O}^{\rm CDW}}{4} \qquad (2)$$

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, α = 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 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. 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.

[1] T. Liamsuwan and H. Nikjoo, Phys. Med. Biol. **58** 641–672 (2013).

[2] O. Mohamad, B. J. Sishc, J. Saha, A. Pompos, A. Rahimi, M. D. Story, A. J. Davis, D. N. Kim, Cancers **9**, 66 (2017).

[3] A. V. Solov'yov, E. Surdutovich, E. Scifoni, I. Mishustin, and W. Greiner, Phys. Rev. E **79**, 011909 (2009);

[4] Denifl S., Mrk T.D., Scheier P. Eds: García Gómez-Tejedor G., Fuss M. Springer, Dordrecht (2012)

[5] N. A. Gafur, M. Sakakibara, S. Sano, K. A. Sera, Water **10**, 1507 (2018); doi:10.3390/w10111507.

[6] D. Benedetti, E. Nunes, M. Sarmento, C. Porto, C. E. Iochims dos Santos, J. Ferraz Dias, J. da Silva, Mutation Research/Genetic Toxicology and Environmental Mutagenesis, Volume 752, 28-33 (2013);

[7] P. de Vera, R. Garcia-Molina,I. Abril, and A. V. Solovyov, Phys. Rev. Lett. 110, 148104 (2013).

[8] A. M. P. Mendez, C. C. Montanari, and J. E. Miraglia, J. Phys. B: At. Mol. Opt. Phys. **53**, 055201 (2020).

[9] M. A. Quinto, J. M. Monti, C. A. Tachino, P. F. Weck, O. A. Fojón, C. Champion, R. D. Rivarola, Rad. Phys. Chem. **167**, 108337 (2020);

[10] H. J. Lüdde, M. Horbatsch and T. Kirchner, J. Phys. B: At. Mol. Opt. Phys. **52**, 195203 (2019).

[11] H. J. Lüdde, M. Horbatsch and T. Kirchner, Eur. Phys. J. B **91**, 99 (2018).

[12] H. J. Lüdde, A. Achenbach, T. Kalkbrenner, H.-C. Jankowiak and T. Kirchner, Eur. Phys. J. D **70**, 82 (2016).

[13] C. Champion, M. E. Galassi, O. Fojón, H. Lekadir, J. Hanssen, R. D. Rivarola, P. F. Weck, A. N. Agnihotri, S. Nandi, and L. C. Tribedi. J. Phys.: Conf. Ser. **373**, 012004 (2012).

[14] R. K. Janev and L. P. Presnyakov J. Phys. B: At. Mol. Opt. Phys. **13**, 4233 (1980).

[15] R. D. DuBois, E. C. Montenegro and G. M. Sigaud, AIP Conference Proceeding **1525**, 679 (2013).

[16] E. C. Montenegro, G. M. Sigaud, and R. D. DuBois, Phys. Rev. A **87** 012706 (2013).

[17] A. Itoh, Y. Iriki, M. Imai, C. Champion, and R. D. Rivarola, Phys. Rev. A **88**, 052711 (2013).

[18] Y. Iriki, Y. Kikuchi, M. Imai, and A. Itoh Phys. Rev. A **84**, 052719 (2011).

[19] W. Wolff, H. Luna, L. Sigaud, A. C. Tavares, and E. C. Montenegro J. Chem. Phys. **140**, 064309 (2014).

[20] M. Wang, B. Rudek, D. Bennett, P. de Vera, M. Bug, T. Buhr, W. Y. Baek, G. Hilgers, H. Rabus, Phys. Rev. A **93**, 052711 (2016).

[21] S. Bhattacharjee, C. Bagdia, M. R. Chowdhury, A. Mandal, J. M. Monti, R. D. Rivarola, and L. C. Tribedi, Phys. Rev. A **100**, 012703(2019).

[22] A. N. Agnihotri, S. Kasthurirangan, S. Nandi, A. Kumar, M. E. Galassi, R. D. Rivarola, O. Fojón, C. Champion, J. Hanssen, H. Lekadir, P. F. Weck, and L. C. Tribedi. Phys. Rev. A **85**, 032711 (2012).

[23] A. N. Agnihotri, S. Kasthurirangan, S. Nandi, A. Kumar, C. Champion, H. Lekadir, J. Hanssen, P. F. Weck, M. E. Galassi, R. D. Rivarola, O. Fojón and L. C. Tribedi, J. Phys. B: At. Mol. Opt. Phys. **46**, 185201 (2013).

[24] H. Luna, A. L. F. de Barros, J. A. Wyer, S. W. J. Scully, J. Lecointre, P. M. Y. Garcia, G. M. Sigaud, A. C. F. Santos, V. Senthil, M. B. Shah, C. J. Latimer, and E. C. Montenegro, Phys. Rev. A **75**, 042711 (2007).

[25] M. A. Bolorizadeh and M. E. Rudd, Phys. Rev. A **33**, 888 (1986).

[26] M. E. Rudd, T. V. Goffe, R. D. DuBois, L. H. Toburen, Phys. Rev. A **31**, 492 (1985).

[27] L. H. Toburen, W. E. Wilson and R. J. Popowich, Radiat. Res. **82**, 27–44 (1980).

[28] D. Ohsawa, Y. Sato, Y. Okada, V. P. Shevelko, and F. Soga Phys. Rev. A **72**, 062710 (2005).

[29] M. E. Rudd, T. V. Goffe, and A. Itoh, Phys. Rev. A **32**, 2128 (1985).

[30] H. Luna, W. Wolff, E. C. Montenegro, Andre C. Tavares, H. J. Ludde, G. Schenk, M. Horbatsch, and T. Kirchner, Phys. Rev. A **93**, 052705 (2016).

[31] C. Dal Cappello, C. Champion, O. Boudrioua, H. Lekadir, Y. Sato, D. Ohsawa, Nuclear Instruments and Methods in Physics Research B 267 (2009) 781–790.

[32] Shamik Bhattacharjee, S. Biswas, J. M. Monti, R. D. Rivarola, and L. C. Tribedi, Phys. Rev A **96**, 052707 (2017).

[33] S. Bhattacharjee, S. Biswas, C. Bagdia, M. Roychowdhury, S. Nandi, D. Misra, J. M. Monti, C. A. Tachino, R. D. Rivarola, C. Champion and L. C. Tribedi, J. Phys. B: At. Mol. Opt. Phys. **49,** 065202 (2016).

[34] M. A. Rahman and E. Krishnakumar, Electron ionization of DNA bases, J. Chem. Phys. **144**, 161102 (2016).

[35] M. U. Bug, W. Y. Baek, H. Rabus, C. Villagrasa, S. Meylan, A. B. Rosenfeld, Rad. Phys. Chem. **130**, 459–479 (2017).

[36] W. Wolff, B. Rudek, L. A. da Silva, G. Hilgers, E. C. Montenegro, M. G. P. Homem, J. Chem. Phys. **151**, 064304 (2019).

[37] M. Fuss, A. Muoz, J. C. Oller, F. Blanco, D. Almeida, P. Limo-Vieira, T. P. D. Do, M. J. Brunger, G. García, Phys. Rev. A **80**, 052709 (2009).

[38] L. Sarkadi, J. Phys. B: At. Mol. Opt. Phys. **49** 185203 (2016)

[39] M. E. Rudd, R. D. DuBois, L. H. Toburen, and C. A. Ratcliffe, T. V. Goffe, Phys. Rev. A **28**, 3244 (1983).

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

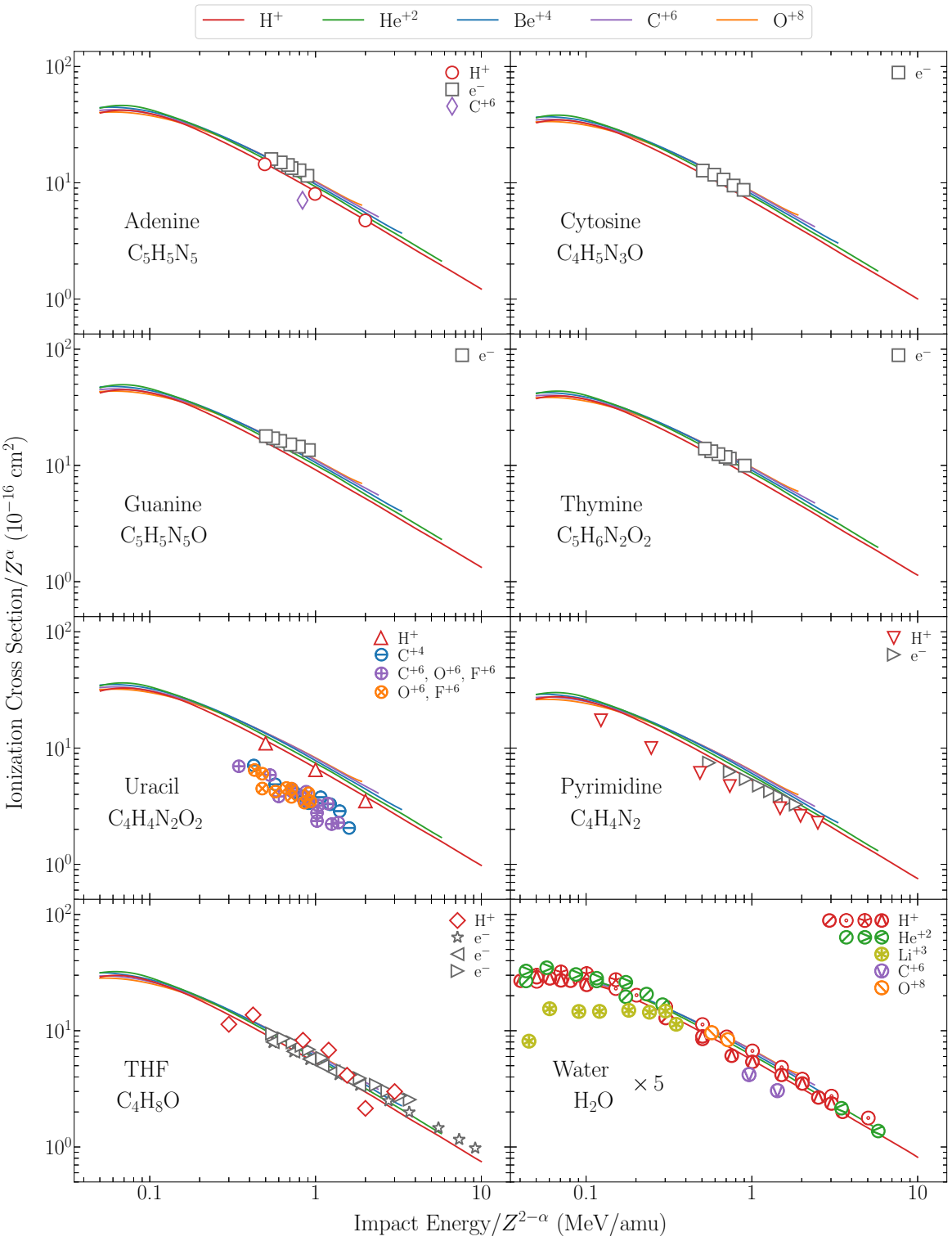

FIG. 1. (Color online) Scaled ionization cross section σ/Z^{α} as a function of ion impact energy $E/Z^{2-\alpha}$ with $\alpha = 1.2$. Colors are associated with the incident ion labeled on top of the figure. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of ○ H^+ [18] and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

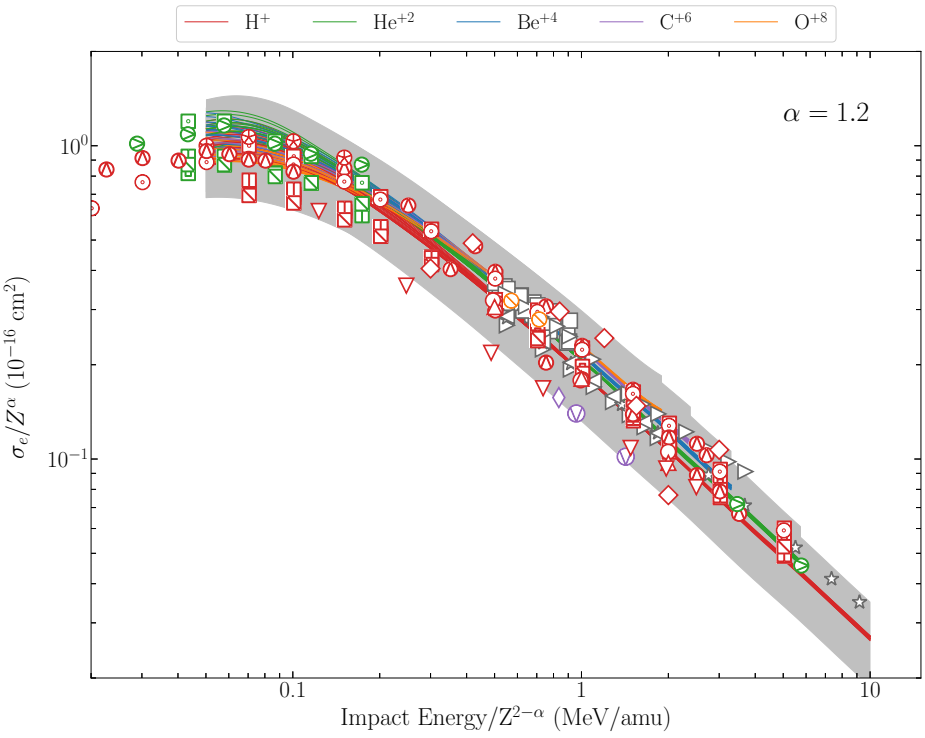

FIG. 2. (Color online) Universal scaling with the ions charge Z and the number of active electrons in the molecule n_e given by Eq. (3) with $\alpha = 1.2$. Curves: present CDW-SSM theoretical results. Symbols: experimental impact of H^+ on ○ adenine [18], △ uracil [17], ▽ pyrimidine [19] and ◇ THF [20];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