Benchmarking Adsorption Energetics and Reaction Mechanisms: Insights in Water–Carbon and H–Si Interfaces

Theodoros Tsatsoulis* and Costas Charitidis

School of Chemical Engineering, National Technical University of Athens, Heroon Polytechniou 9 15773, *tsatsoulis@chemeng.ntua.gr

Key Words: *Electronic Structure Theory, Surface Chemistry, Molecular Adsorption and Dissociation, Reaction Pathways, Carbon Nanotube Growth, Computational Methods.*

Abstract

The adsorption and diffusion of molecules on surfaces play a crucial role in applications such as catalysis, gas storage, water purification, and nanostructure growth and synthesis. In particular, water–carbon interfaces exhibit unique properties, including near-frictionless flow on sp^2-bonded carbon surfaces like graphene and carbon nanotubes, while hexagonal boron nitride (h-BN) surfaces behave differently. Understanding the fundamental nature of molecular adsorption, including bond strength and interaction mechanisms, is essential for advancing these applications. In the poster, high-level ab initio benchmarks for adsorption energies of water on BN and graphene surfaces[1,2] are presented, employing coupled-cluster theory, diffusion Monte Carlo, MP2, and RPA-based methods. Static polarizabilities and dispersion coefficients derived from TD-DFT and MBD reveal significant non-additive dispersion interactions, highlighting the importance of anisotropy in low-dimensional materials. For the dissociative adsorption of H_2 on Si(100)[3], a periodic CCSD(T) study is presented that accurately reproduces experimental adsorption barriers and reaction energies, overcoming limitations of DFT-GGA and meta-GGA functionals that suffer from self-interaction errors. Hybrid functionals, such as PBE0 and HSE06, provide reasonable approximations but tend to slightly underestimate adsorption barriers. These findings demonstrate the necessity of benchmarking electronic structure theories against high-level wavefunction methods to ensure predictive accuracy. Building on this foundation, future work will explore atomistic insights into carbon nanotube (CNT) growth, from precursor adsorption and dissociation to predictive modeling of growth pathways[4].

References

[1] Jan Gerit Brandenburg, Andrea Zen, Martin Fitzner, Benjamin Ramberger, Georg Kresse, Theodoros Tsatsoulis, Andreas Grüneis, Angelos Michaelides, and Dario Alfè
The Journal of Physical Chemistry Letters 2019 10 (3), 358-368
[2] Yasmine S. Al-Hamdani, Mariana Rossi, Dario Alfè, Theodoros Tsatsoulis, Benjamin Ramberger, Jan Gerit Brandenburg, Andrea Zen, Georg Kresse, Andreas Grüneis, Alexandre Tkatchenko, Angelos Michaelides; Properties of the water to boron nitride interaction: From zero to two dimensions with benchmark accuracy. J. Chem. Phys. 28 July 2017; 147 (4): 044710.
[3] Theodoros Tsatsoulis, Sung Sakong, Axel Groß, Andreas Grüneis; Reaction energetics of hydrogen on Si(100) surface: A periodic many-electron theory study. J. Chem. Phys. 28 December 2018; 149 (24): 244105.

[4] Page, A. J., Ding, F., Irle, S., & Morokuma, K. (2015). Insights into carbon nanotube and graphene formation mechanisms from molecular simulations: a review. Reports on Progress in Physics, 78(3), 036501.