



Review article

Adsorption structures and energetics of molecules on metal surfaces: Bridging experiment and theory



Reinhard J. Maurer^{a,b}, Victor G. Ruiz^c, Javier Camarillo-Cisneros^c, Wei Liu^d, Nicola Ferri^c, Karsten Reuter^b, Alexandre Tkatchenko^{c,e,*}

^a Department of Chemistry, Yale University, New Haven, CT06520, United States

^b Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany

^c Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

^d Nano Structural Materials Center, School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing210094, Jiangsu, China

^e Physics and Materials Science Research Unit, University of Luxembourg, L-1511, Luxembourg

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ABSTRACT

Adsorption geometry and stability of organic molecules on surfaces are key parameters that determine the observable properties and functions of hybrid inorganic/organic systems (HIOSs). Despite many recent advances in precise experimental characterization and improvements in first-principles electronic structure methods, reliable databases of structures and energetics for large adsorbed molecules are largely amiss. In this review, we present such a database for a range of molecules adsorbed on metal single-crystal surfaces. The systems we analyze include noble-gas atoms, conjugated aromatic molecules, carbon nanostructures, and heteroaromatic compounds adsorbed on five different metal surfaces. The overall objective is to establish a diverse benchmark dataset that enables an assessment of current and future electronic structure methods, and motivates further experimental studies that provide ever more reliable data. Specifically, the benchmark structures and energetics from experiment are here compared with the recently developed van der Waals (vdW) inclusive density-functional theory (DFT) method, DFT + vdW^{surf}. In comparison to 23 adsorption heights and 17 adsorption energies from experiment we find a mean average deviation of 0.06 Å and 0.16 eV, respectively. This confirms the DFT + vdW^{surf} method as an accurate and efficient approach to treat HIOSs. A detailed discussion identifies remaining challenges to be addressed in future development of electronic structure methods, for which the here presented benchmark database may serve as an important reference.

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* Corresponding author at: Physics and Materials Science Research Unit, University of Luxembourg, L-1511, Luxembourg.

E-mail address: tkatchenko@fhi-berlin.mpg.de (A. Tkatchenko).

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1. Introduction

The interaction of organic materials and molecules with metal surfaces is of widespread interest to both fundamental science and technology. The eventual control of the functionality of the formed hybrid inorganic–organic systems (HIOSs) has potential applications to a variety of fields ranging from functionalized surfaces, to organic solar cells [1], molecular electronics [2], nanotechnology [3,4], and medical implantology [5]. A bottom-up approach of molecular nanotechnology promises a potential route to overcome size limitations of nanoscale devices constructed with traditional top-down approaches such as lithography based device design. An important prerequisite to such an approach is the ability to control and manipulate the structure and interactions of individual molecular building blocks mounted on well-defined surfaces. This can only be achieved with the expertise to fully characterize the adsorption geometry and fully understand the, sometimes subtle, interplay of interactions that lead to a particular molecule–substrate binding strength.

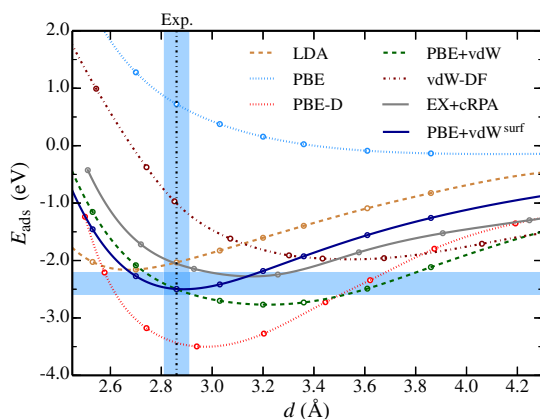


Fig. 1. Adsorption energy curve of PTCDA adsorbed at Ag(111). Shown are the results of different DFT methods and dispersion correction approaches. Experimental results from X-ray standing wave measurements [16] and estimated from TPD data of the smaller analogue molecule NTCD [14,17] are shown as blue bars. A detailed analysis of this figure can be found in Section 4. Based on Fig. 1 of Ref. [17].

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