Research paper

Tuning dispersion correction in DFT-D2 for metal-molecule interactions: A tailored reparameterization strategy for the adsorption of aromatic systems on Ag(1 1 1)

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ABSTRACT

Common local and semi-local density functionals poorly describe the molecular physisorption on metal surfaces due to the lack of dispersion interactions. In the last decade, several correction schemes have been proposed to amend this fundamental flaw of Density Functional Theory. Using the prototypical case of aromatic molecules adsorbed on Ag(1 1 1), we discuss the accuracy of different dispersion-correction methods and present a reparameterization strategy for the simple and effective DFT-D2. For the adsorption of different aromatic systems on the same metallic substrate, good results at feasible computational costs are achieved by means of a fitting procedure against MP2 data.

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1. Introduction

Since the pioneering articles of Zaremba and Kohn [1], it became rather evident that the description of physisorption on metal surfaces cannot leave apart the proper account of dispersion interactions. Today the most widely used approaches to study metal-organic interfaces are derived from the Density Functional Theory (DFT), it is well known that local and semi-local implementations of the exchange-correlation (xc) functional are unable to catch the essence of dispersion forces [2]. In fact, many-body perturbation theory (MBPT) and coupled cluster techniques are the methods of choice to obtain an accurate prediction of van der Waals forces [3], but the huge computational demand of MBPT-derived approaches prevents their application to large systems. The inclusion of dispersion forces within the framework of DFT allows the accurate prediction of a variety of chemical systems while exploiting the computational effectiveness of the DFT codes.

In the last decade, to correct this deficiency of DFT different research groups have proposed several methods that provide powerful tools for studying van der Waals complexes [4] and soft materials [5]. Among them, the semi-empirical dispersion-correction

scheme developed by Grimme [6] (DFT-D2) is certainly the most largely used, mainly because of its computational efficiency and the widespread availability on almost all the DFT codes. It consists in a pairwise atom-atom potential in the common form $C_6 \times r^{-6}$ potential weighted by a damping function that shuts off the interaction between directly bonded atoms. There, the C_6 coefficients are computed by using a square root combination rule on atomic coefficients, which in turn are obtained from DFT calculations of polarizabilities and ionization potentials of the isolated atoms. The newest implementation of the Grimme approach (DFT-D3) [7] shares with the former the $C^6 \times r^{-6}$ form, but the C_6 coefficients are obtained from Time-Dependent (TD) DFT calculations and the combination rule takes into account of the atom connectivity, i.e. the molecular topology. A completely different scheme was proposed by Dion et al. [8,9], who developed a non-local correlation functional (vdw-DF) to model the long-range correlation that gives rise to dispersion forces. Unfortunately, when applied to the case of organic molecules physisorbed on metal surfaces, all the aforementioned methods give only moderate improvement with respect to the DFT picture. In particular, both the DFT-D2 and the DFT-D3 approaches overestimate the dispersion interaction at the metal-organic interface [7], although the latter partly corrects this behavior. Besides, the vdw-DF functional provides better values for the adsorption energy, but overestimates the metal-molecule distance [10]. Several subsequent refinements of

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vdW-DF were proposed over the years, including a vdW-DF2 [11–13] by the same developers, a revised version of the latter [14] and a method by Tkatchenko and Sheffler that is based on the summation of interatomic coefficients, obtained from the electron density of the molecule (or solid) and accurate reference data for the free atoms [15]. More approaches to include dispersion in DFT have been recently proposed and a full survey of the merits and limits of these new schemes is beyond the purpose of this Letter, but we refer the interested reader to some recent thorough reviews on this topic [16,17]. As a general trend, the more accurate and physically sound models are implemented the more the computational burden increases. Recently, Román-Peréz and Soler proposed an efficient implementation of the non-local vdW-DF functionals with twice the computational costs of standard semi-local DFT calculations [18]. However, these costs still prevent the application of the most recent non-local dispersion corrected DFT for describing complex large systems of hybrid and heterogeneous materials.

On the other hand, thanks to its simple functional form, the DFT-D2 scheme can be modified *ad hoc* to fit experimental and/or accurate computational results. For example, recently Robledo et al. in Ref. [19] proposed to apply the D2 correction only for metal atoms at the topmost layer of the surface in order to account for the screening effect of metals. However, such approach is too system specific to be easily transferred to other systems or to reconstructed surfaces.

With the aim of making DFT-D2 suitable for large scale calculations that include dispersion interactions at surfaces, we report a reparameterization scheme (hereafter DFT-D2s) on the case study of molecular adsorption on silver: the van der Waals radius of Ag was modified to fit MP2 data on a cluster model of the Ag(1 1 1) surface decorated by benzene and three heterocyclic aromatic molecules. We tested the modified DFT-D2s on a different computational approach that relies on periodic boundary conditions (PBC) and considering the adsorption of benzene and phthalocyanine (H$_2$Pc) molecules on the extended Ag(1 1 1) surface slab. As a prototypical model for the metal-organic interface, the Ag(1 1 1)/C$_6$H$_6$ system was studied extensively in the past by means of a variety of experimental [20–24] and computational techniques [25–27]. In particular, the desorption energy E$_{des}$ of the C$_6$H$_6$ monolayer (ML) are known from Temperature-Programmed Desorption (TPD) experiments [24] alongside with workfunction measurements [22]. The desorption energy was reported by T. J. Rockley et al. (E$_{des}$ = 0.37 eV) and it can be directly compared to the opposite of the adsorption energy E$_{ads}$ defined above, while the workfunction change upon adsorption of benzene on Ag(1 1 1) amounts to −0.7 eV [22]. DFT-D2s results on the periodic model of the Ag(1 1 1) surface covered by one ML of C$_6$H$_6$ are then compared to other dispersion-corrected DFT schemes as well as to these experimental data. Finally, the DFT-D2s scheme is successfully applied to the study of the adsorption of metal-free phthalocyanine H$_2$Pc on the same substrate.

2. Computational details

MP2 and DFT calculations were performed with the Gaussian package [28] on a cluster model of the Ag(1 1 1) surface functionalized by either benzene, pyridine, furan or thiophene. To represent the Ag(1 1 1) surface we adopted the Ag$_{32}$ cluster proposed by Caputo et al. [25], which has been carved out by the experimental lattice bulk using the lattice constant a_{Ag} equal to 4.09 Å [29]. This gas-phase cluster model has been extensively used to model the interaction between aromatic molecules and coinage metals at the MP2 level of theory [30,31]. A fair agreement with experimental adsorption lengths and energies was found and so the model has been taken as a reference for the adsorption of aromatic mole-

cules on metals in recent dispersion-corrected DFT investigations [32–34]. Here MP2 calculations on the Ag$_{32}$ cluster model are used as benchmark for our re-parameterization procedure. This level of theory has been extensively applied in finite-size metal clusters [25,30,31] and it has been also successfully tested against higher levels of theory [36], allowing us to consider it reliable for the adsorption of aromatic molecules on the Ag cluster. Fig. 1 depicts the minimum-energy structures of the adsorbed molecules and of the model cluster. A Stuttgart RCS (Relativistic Small Core) 1997 basis set with Effective Core Potential (ECP) was used for Ag, while C and H were described through an all-electron 6-311+ +G(d,p) basis set. DFT calculations were carried out by using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation density functional [35].

The default van der Waals radius of Ag was then modified to fit the MP2 data. The resulting DFT-D2s scheme was employed for the study of a full ML of the aromatic molecules adsorbed on Ag(1 1 1) surface, where fully periodic calculations were carried out on slab models of the Ag surface using the Quantum-ESPRESSO [37] package. Valence orbitals were expanded on a plane-wave basis set with kinetic energy cutoff of 25 Ry, while the cutoff on the augmentation density was 300 Ry, and the interaction between ion cores and valence electrons was modeled by ultra-soft pseudopotentials [38]. The periodic model of the Ag(1 1 1) surface was an asymmetric slab containing 6 atomic layers, where benzene was adsorbed only on one side and a hexagonal 3 × 3 cell was used to reproduce the close-packed phase formed by C$_6$H$_6$ on Ag(1 1 1) [20]. The length of the cell along the z axis ensures a distance between repeated images larger than 15 Å. The reciprocal space was sampled with a Γ-centered 8 × 8 mesh, which consists in 34 irreducible k-points in the first Brillouin zone, 0.02 Ry of cold smearing [39] were applied to the electron population function, and a dipole-correction scheme [40] was employed to remove the spurious potential drift arising from the slab asymmetry. The Ag(1 1 1) surface was relaxed once and then kept frozen upon adsorption of benzene. With this set-up total energies are converged within 1 meV. Adding a seventh layer of Ag atoms to the metal slab changes the adsorption energy of C$_6$H$_6$ no more than 1 meV. The dispersion correction terms DFT-D2, DFT-D2s, and DFT-D3 were computed on-top of the PBE results using a modified version of the dftd3 code [41], where periodic conditions were implemented; vdw-DF results were obtained using the same setup, while the exchange term was given by the revPBE formula [42]. To test the transferability of the DFT-D2s approach, an ordered ([5 0; 3 6]) phase of H$_2$Pc was simulated. The model cell (see Fig. 3) contains 6 atomic layers of Ag, each composed by 30 atoms, and a H2Pc molecule adsorbed on one side of the slab. A Γ-centered 2 × 2 k-point integration scheme was used.

For each system, adsorption curves were produced by means of rigid scans of the distance between the slab top layer and the plane of the molecule lying flat, parallel to the surface. The adsorption energy E$_{ads}$ of the aromatic molecules on Ag(1 1 1) was computed as the difference between the total energy of the adsorbed system E$_{sys}$ and the sum of the total energies of the surface model E$_{Ag}$ and of the molecule E$_{mol}$:

$$E_{ads}(d_H) = E_{sys}(d_H) - (E_{Ag} + E_{mol}). \qquad (1)$$

Adsorption energies obtained with the Gaussian code were all corrected for the basis set superposition error by means of the counterpoise method [43].

3. Results and discussion

The first part of the work consisted of testing and refining the DFT-D2 parameter for Ag by studying the adsorption of four molecules on the Ag$_{32}$ model of the Ag(1 1 1) surface (Fig. 1).
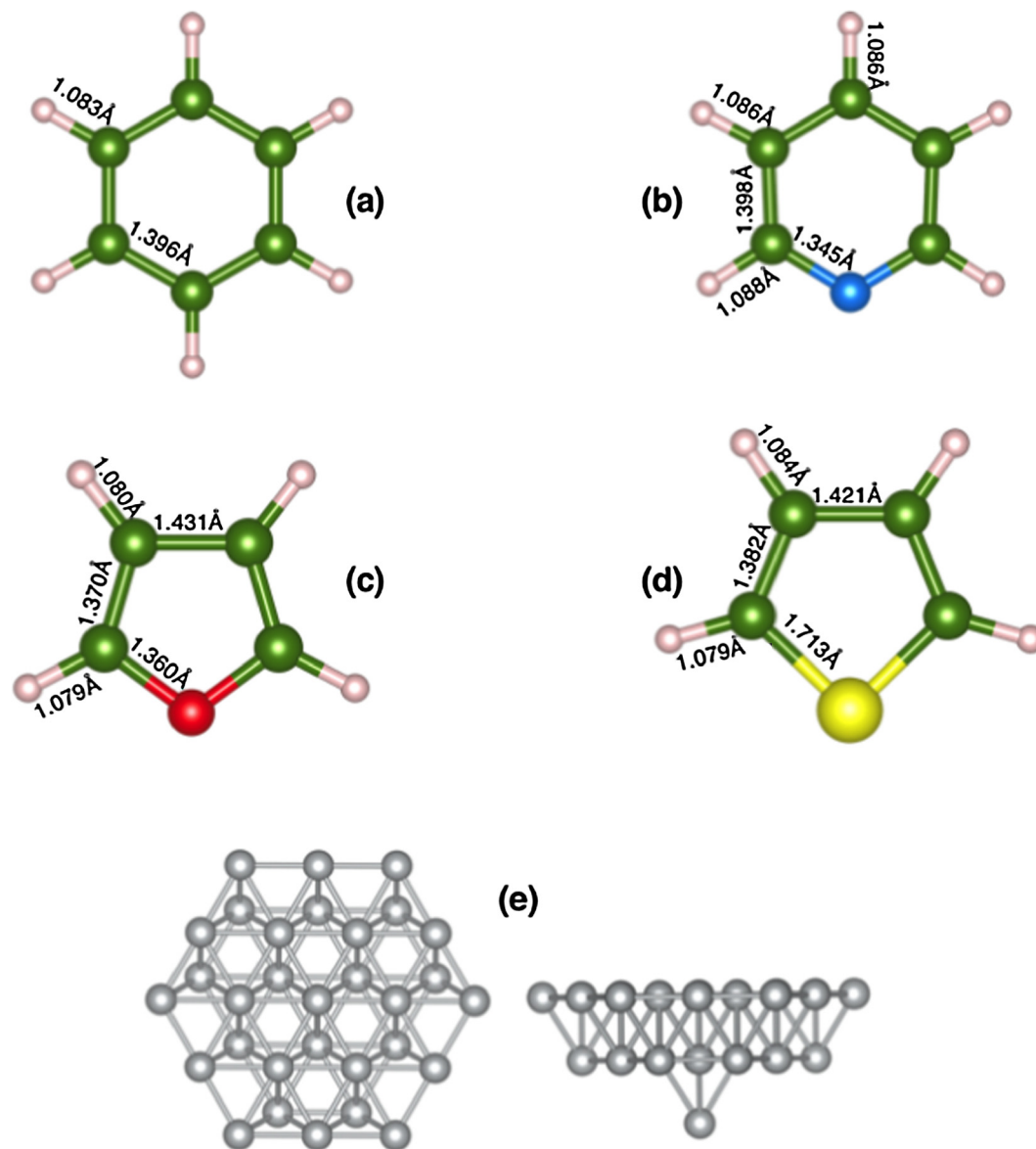
Fig. 1. Structure and bond lengths of (a) benzene, (b) pyridine, (c) furan and (d) thiophene; (e) top (left) and lateral (right) view of the Ag_{32} cluster build from the Ag fcc bulk structure (a_0 = 4.090 Å) and representative of the Ag(1 1 1) surface.

We used MP2 as a benchmark and we tested various combinations of the Ag C_6 and R_{vdW} parameters on the four systems. We focused on the adsorption energies and the minimum-energy distances, evaluating the Mean Absolute Errors and Mean Absolute Percentage Errors (MAPE) with respect to the MP2 counterparts. By lowering the Ag C_6 parameter we obtained as expected a decrease in the adsorption energy values, but the position of the minima were not affected, leading always to lower equilibrium distances than MP2 values. By increasing the Ag R_{vdW} parameter we obtained the desired effect of lowering the adsorption energies and, at the same time, moving the minimum-energy distances further from the surface. The different behaviors between changes of C_6 and R_{vdW} are due to the DFT-D2 formulation, where the C_6 parameter is important for the strength of the dispersion interaction, while the R_{vdW} acts on the damping function that quenches the dispersion interaction at short ranges. Increasing the R_{vdW} value allows to reduce the extent of the vdW interaction by switching off the dispersion at longer interatomic distances.

The use of the original DFT-D2 Ag C_6 parameter and the increase of the Ag R_{vdW} parameter by 65% provided the best combination for

lowering the errors on both energies and distances. Fig. 2 shows the adsorption curves for the four molecules and the corresponding MAPE values.

To validate the transferability of the revised DFT-D2s parameters, we performed a PBC study on benzene and phthalocyanine molecules adsorbed on the Ag(1 1 1) surface slab model, as depicted by Fig. 3. Periodic calculations on the Ag(1 1 1)/C_6H_6 system were performed with the molecule sitting either on-top of an Ag surface atom (OT) or on a hollow site (H), either oriented with two C—H bonds pointing along the $[\bar{1}\,\bar{1}\,2]$ (OT-A and H-A) or the $[1\,\bar{1}\,0]$ (OT-B and H-B) Ag(1 1 1) surface direction (see Fig. 3).

According to experimental findings, all the exploited methods predicted the stable site to be H, while the impact of the orientation of the C_6H_6 units is negligible. Table 1 lists the adsorption energies and the surface-molecule equilibrium distances obtained by means of different computational approaches, namely the DFT-D2, DFT-D3 and DFT-D2s schemes and the vdW-DF functional. As in the case of the Ag_{32}-C_6H_6 system, both DFT-D2 and DFT-D3 overestimated the ML formation energy, while the DFT-D2s approach gives overall better agreement between theory and experiment.
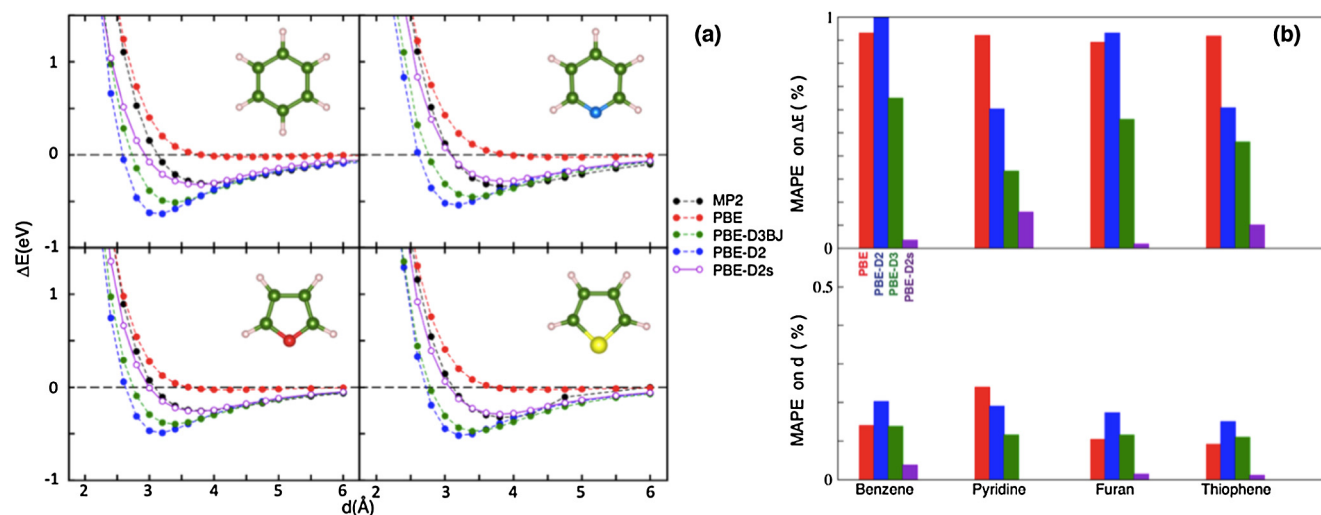
Fig. 2. (a) Potential energy surface scan for the parallel adsorption of the aromatic molecules on the Ag$_{32}$ cluster top surface; (b) Mean Absolute Percentage Error (MAPE) with respect to MP2 considering the binding energy (top panel) and the minimum-energy distance (bottom panel).
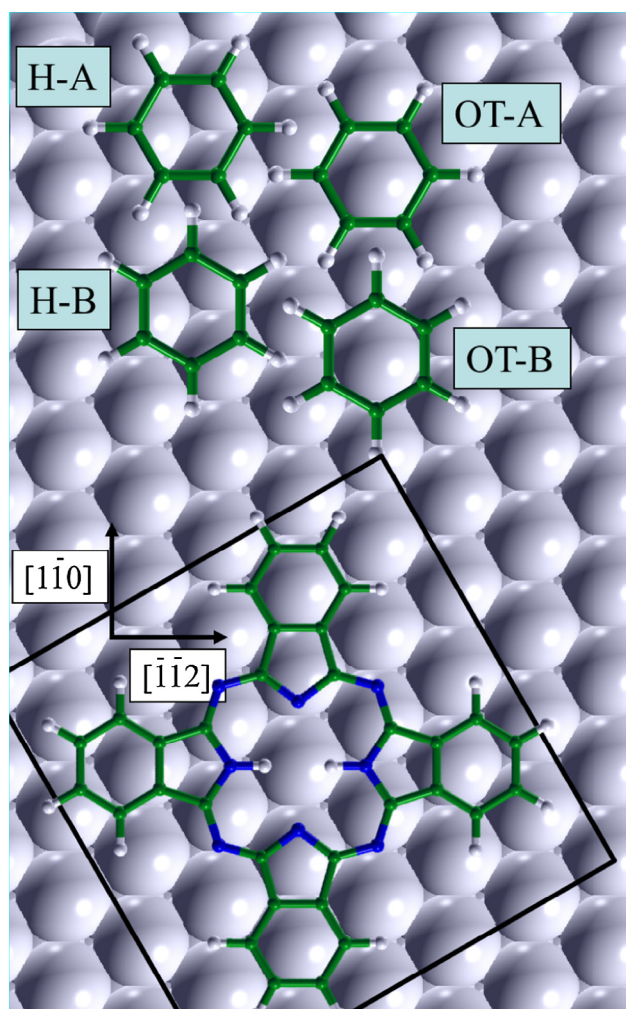

Fig. 3. The four adsorption geometries of the C$_6$H$_6$ on Ag(1 1 1) and the on-top H$_2$Pc molecule. Selected surface directions are shown alongside with the simulation cell of the H$_2$Pc covered surface.

In accordance with previous calculations [27], the non-local dispersion functional vdW-DF gives a fairly accurate value of E$_{ads}$ = −0.52 eV.

The work function Φ of functionalized metal surfaces is very sensitive to the metal-molecule distance d$_H$, thus providing a way to estimate the latter from computational outcomes. Work function changes (ΔΦ) were computed as difference between the vacuum level of the functionalized surface and that of the bottom side of the slab. A detailed analysis of the computed ΔΦ trend is beyond the purpose of the present work and can be found elsewhere (see for example Ref. [19] and references therein). The experimental metal-molecule distance was deduced to be 3.0 Å, as the computed ΔΦ perfectly agrees with the experiment when d$_H$ takes this value. The PBE-D2 minimum shows good agreement with the experimental d$_H$, while PBE-D2s and PBE-D3 predict a slightly longer distance. Pure PBE and vdW-DF calculations perform even worse, overestimating d$_H$ by 0.8 and 0.6 Å, respectively.

To further test the transferability of the refined Ag DFT-D2s parameter, we studied the adsorption of the metal-free phthalocyanine on Ag(1 1 1). For this system, Scanning Tunneling Microscopy (STM) and Temperature Programmed Desorption (TPD) experiments have been reported in literature [39,44]. The desorption temperature obtained through TPD experiments (705 K) was used here to estimate the desorption energy (E$_{des}$) of a H$_2$Pc molecule, by either assuming a first-order desorption kinetic through the Redhead equation [45] (the pre-exponential factor was set to the usual value of 10^{13}), or a zero-order kinetic, by means of the procedure proposed by Wagner et al. [46]. The two methods give a fairly narrow interval of E$_{des}$ = 1.76 ÷ 2.00 eV, where the lower (upper) bound has been obtained by adopting a zeroth- (first-) order kinetic model. H$_2$Pc molecules on Ag(1 1 1) self-organize in a coverage-dependent structure, but tend to form a commensurate ([5 0; 3 6]) phase when the limit of 1ML is reached [47]. We modeled the full monolayer using the supercell previously described and depicted in Fig. 3, where molecules may be adsorbed on i) an OT site, ii) on a H site or iii) on a bridge site (B) with two lobes oriented along the [1 1̄ 0] direction, as depicted by Fig. 3b. The most stable site was found to be H, although ΔE$_{ads}$ between different sites are rather small (see Table 2).

The PBE-D2s method predicts an adsorption energy of 1.72 eV for the most stable site and an equilibrium surface-molecule distance of 3.7 Å. Direct measurement of the metal-molecule distance by means of normal incidence X-ray standing wave (NIXSW) technique done by Kröger et al. [47] provided a d$_H$ value of ∼3.07 Å, significantly shorter than the prediction of DFT-D2s. However, the predicted work function change ΔΦ = −0.23 eV matches the

Table 1

Adsorption energies E_{ads} (eV), metal-molecule distances d_H (Å), and workfunction changes $\Delta\Phi$ (eV) as obtained from different computational schemes for benzene (see Fig. 3). Experimental values are reported for comparison.

		PBE	PBE-D2	PBE-D3	vdW-DF	PBE-D2s	Exp
OT-A	E_{ads}	−0.05	−0.88	−0.66	−0.50	−0.42	–
	d_H	4.0	3.0	3.2	3.8	3.6	–
	$\Delta\Phi$	−0.15	−0.65	−0.52	−0.22	−0.30	
OT-B	E_{ads}	−0.05	−0.87	−0.65	−0.50	−0.42	–
	d_H	4.0	3.0	3.2	3.8	3.6	–
	$\Delta\Phi$	−0.16	−0.67	−0.53	−0.22	−0.31	–
H-A	E_{ads}	−0.05	−0.93	−0.71	−0.52	−0.47	−0.37[a]
	d_H	3.8	3.0	3.2	3.6	3.4	3.0[b]
	$\Delta\Phi$	−0.24	−0.70	−0.55	−0.34	−0.43	−0.7[c]
H-B	E_{ads}	−0.05	−0.94	−0.72	−0.52	−0.47	–
	d_H	3.8	3.0	3.2	3.6	3.4	–
	$\Delta\Phi$	−0.23	−0.69	−0.55	−0.34	−0.43	–

[a] From Ref. [24].
[b] Deduced from the work-function change.
[c] From Ref. [22].

Table 2

PBE-D2s adsorption energies E_{ads} (eV) and molecule-metal distances d_H (Å) of H_2Pc adsorbed on different sites of the Ag(1 1 1) surface.

	d_H	E_{ads}
OT	3.7	−1.60
H	3.7	−1.72
B	3.7	−1.68

results of Caplins et al. [48], who measured a work function of 4.2 eV for the H_2Pc ML on Ag(1 1 1), corresponding to a $\Delta\phi$ of −0.2(6) eV with respect to the clean Ag(1 1 1) surface [49]. This discordance may partly arise from different sample preparation in the two cases, and in particular from the surface coverage. Caplins et al. measurements are performed at 1ML coverage, whereas Kröger et al. measurements span a lower coverage interval, namely from 0.7 to 0.93 ML. Our calculations matches better with experimental outcomes from Caplins et al. because our model is a better representation of the fully covered surface. Indeed, NIXSW show that the molecule height is sensitive to the surface coverage: on passing from 0.7 ML to a 0.93 ML, the height of N atoms raises of 0.2 Å. A further increase of the coverage close to the physical limit of 1 ML, may speed up the process, due to the growing role of surface-mediated repulsion [30].

Overall, DFT-D2s represents a significant improvement over both the DFT-D2 and the DFT-D3 method, and the fitting procedure against MP2 data proposed here provides a route to extract a set of parameters that correct the over-binding tendency of the named methods at the metal/organic interfaces.

4. Conclusions

This study presents a viable strategy to tune the DFT-D2 parameters for metals in order to achieve a qualitatively reliable description of metal-molecule interaction. We used MP2 cluster calculations and refined the silver parameters testing the planar physisorption of benzene and other three different heterocyclic aromatic molecules on a Ag_{32} model of the Ag(1 1 1) surface. We aimed at finding a balanced description of interaction energies and equilibrium distances: our fitting procedure resulted in an increased R_{vdW} value by 65% with respect to the original DFT-D2 value. The larger vdW radius effectively reduces the strength of the dispersion interaction, thus correcting the well-known DFT-D2 overbinding tendency for physisorption of molecules on silver surfaces at no additional computational costs.

We then tested our revised DFT-D2s for PBC calculations on extended Ag(1 1 1) surface slab model. Our study confirms that the PBE-D2 semi-empirical dispersion correction overbinds the benzene molecule to the metal surface. While the adsorption energy computed by PBE-D3 calculations is in close agreement with the experimental equilibrium distance, it still shows the tendency to overestimate the interaction energy. In contrast to that, the non-local vdw-DF improves the description of dispersion interactions at the interface, but it overestimates the metal-molecule distance. The use of the Ag radius fitted against MP2 data provides the best compromise, allowing a good description of both the stability and the geometry of the C_6H_6/Ag(1 1 1) interface. By applying the DFT-D2s to the study of the interaction between the metal-free phthalocyanine and the Ag(1 1 1) surface we demonstrate the transferability of the new Ag parameter to periodic surfaces interacting with benzene and with a large molecular system. We note that a complete and exhaustive validation of DFT-D2s on an extended set of systems is needed. To this end, our ongoing efforts are devoted to extensive tests of DFT-D2s considering as benchmark the large database recently proposed by Silbaugh and Campbell [50].

In conclusion, we believe that the proposed strategy can be easily applied to other metallic systems and it can circumvent the computational costs of more refined non-local density functionals for qualitative studies of complex heterogeneous systems like the 2D hetero-interface between graphene, h-BN, phosphorene and transition metals that are applied as functional substrates.

Acknowledgments

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