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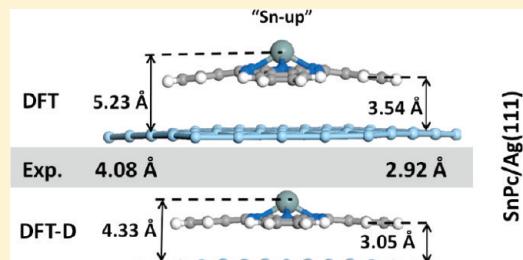
Jakub D. Baran*,†,‡ and J. Andreas Larsson†

†Tyndall National Institute, University College Cork, Lee Maltings, Prospect Row, Cork, Ireland

‡Competence Centre for Catalysis and Department of Applied Physics, Chalmers University of Technology SE-41296 Göteborg, Sweden

S Supporting Information

ABSTRACT: The reversible switch between two electronically and/or geometrically distinct states of a single molecule adsorbed on a well-characterized substrate is of high technological interest due to its possible use as single molecule devices and novel molecular memories. We have studied shuttlecock-shaped metal phthalocyanines, which can adsorb on surfaces in two distinct adsorption configurations, depending on if the central metal atom points toward or away from the surface, and we report on the adsorption of tin-phthalocyanine (SnPc) on an Ag(111) surface using density functional theory (DFT) including a semiempirical dispersion correction (DFT-D). We discuss the binding mechanism in detail and show that the adsorption of SnPc in these two orientations is driven by very different interactions. While “Sn-down” adsorption involves chemical bonding between Sn and the surface (chemisorption), the “Sn-up” configuration is bound only by weak van der Waals forces (physisorption). By comparing our theoretical results with a broad range of experimental data, we assess the effect of dispersion forces for the SnPc/Ag(111) system and how these impact adsorption energies, geometries, and the electronic structure. We show that an inclusion of dispersion forces improves the adsorption geometry with respect to experiment and is essential in order to capture the subtle electronic effects at molecule–metal interfaces. By analyzing the geometric and electronic structure of the adsorbed molecules we, in addition, shed light on the surprising 2-fold symmetry reduction of metal phthalocyanine molecules that has been observed upon adsorption on surfaces.



I. INTRODUCTION

Metal phthalocyanines (MPc, where M refers to the metal and Pc to the phthalocyanine ligand) are metallorganic molecules, structurally similar to important biomolecules such as hemoglobin and chlorophyll. MPc's play an important role in the study of organic–inorganic interfaces and, more specifically, in the field of molecular electronics. These molecules have opto-electronic properties that can be widely varied;¹ they are thermally stable and can easily be sublimated,² and often form well-ordered assemblies on a range of substrates.^{3–5} By varying the central metal atom, the molecular properties of MPc's can be tuned without adding functional groups. In general, MPc's are planar. If, however, the central metal is too large to fit completely into the central cavity, it adopts a position out of the plane of the Pc macrocycle and significant “doming” occurs, giving these molecules a shuttlecock shape (see Figure 1). Because of this shape, shuttlecock-shaped MPc molecules adsorb on metal surfaces in two configurations — either having the central metal atom toward (down) or away from (up) the surface. A reversible switch between these two different configurations can be triggered as a small but energetic nanomechanical motion, with possible use as molecular switches and memories, and sensors at the nanoscale.⁶ An

example of such a system is studied here: the tin-phthalocyanine (SnPc) molecule on the Ag(111) surface. It has been recently demonstrated that the controllable switching between the “Sn-up” and “Sn-down” adsorption configuration of a single SnPc molecule on Ag(111) can be achieved by the use of a scanning tunneling microscope (STM) tip.^{7,8}

The progress in optimizing molecular electronic devices based on MPc molecules requires a detailed understanding of all the relevant chemical and physical processes at the MPc/substrate interface. This particularly concerns the overlap between MPc and surface wave functions that has a key role in the performance of devices because it determines their critical parameters such as the electronic transport.⁹

Although a considerable amount of experimental work has been devoted in recent years toward understanding of the SnPc/Ag(111) system^{5,8,10–13} there are still a number of important issues unresolved, such as the detailed molecular configuration of the MPc/substrate system, the nature of hybridization between molecule and the surface, and

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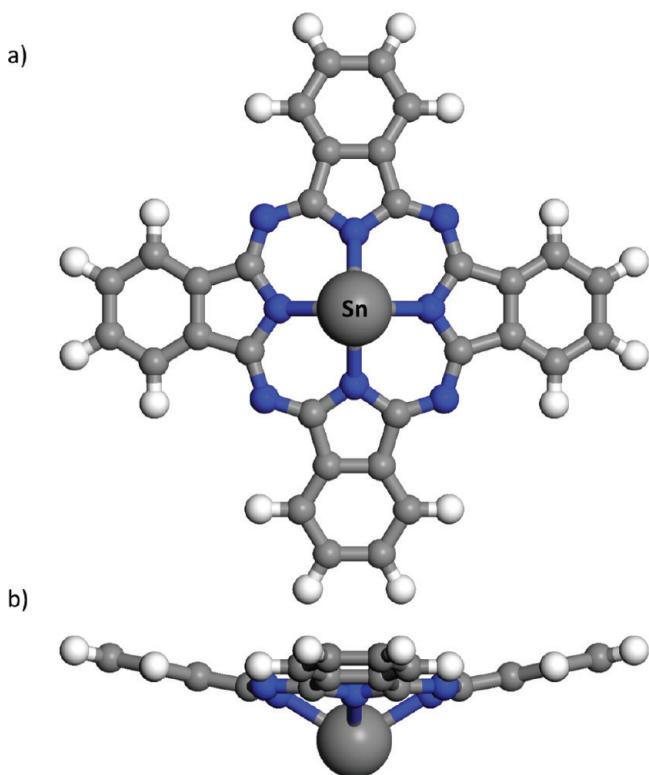


Figure 1. SnPc molecule. (a) Top view, (b) side view. Small gray atoms are C; blue and white atoms are N and H.

molecule–substrate charge transfer. Particularly, the MPC/substrate interaction is still under debate, especially regarding the nature of the interaction (i.e., chemisorption/ physisorption), and the role of the central metal atom and the macrocycle. It is believed that the macrocycle and the central metal atom of MPC's interact with the surface by two different bonding mechanisms.¹⁴ The metal atom usually represents the reactive site of the molecule and can form covalent and/or coordinate bonds, whereas the ligand is less reactive and interacts with the surface by van der Waals (vdW) forces. These issues can, at least in principle, be addressed by electronic structure theory computations. Theoretical models that are able to capture a range of interactions from strong chemisorption to weak physisorption, which are present in these systems, is therefore of high scientific and technological interest.

The nature of the interactions between MPC's and the surface is complex and its fundamental understanding also constitutes a challenge because (i) the high computational demand of

carrying out such calculations for systems of this size and complexity makes the use of methods beyond standard density functional theory (DFT) (e.g., random phase approximation or coupled cluster theory) unrealistic at present; and (ii) the lack of proper description of the vdW interactions in present exchange correlation (XC) functionals makes the use of DFT questionable to describe the portion of binding due to physisorption in these systems. In order to account for the missing dispersion effects in the standard implementation of DFT, several approaches have been proposed, which were recently discussed in the review by Tkatchenko et al.¹⁵ In this work we use the computationally inexpensive semiempirical dispersion correction scheme to standard DFT proposed by Grimme¹⁶ (DFT-D2 method) to study the adsorption of SnPc on the Ag(111) surface. For a detailed description of the computational methods used in this work, see the Computational Methods section below.

By comparing our DFT and DFT-D results with experimental data, we demonstrate the advantages of DFT-D, showing that dispersion interactions make a large contribution to the geometry and, indirectly, to the electronic structure of a MPC/metal interface. Their inclusion in the calculations improves, or is even sometimes essential to obtain agreement with experimental findings for the SnPc/Ag(111) system. We discuss the mechanism of adsorption of a single SnPc molecule on the Ag(111) surface with Sn facing *down* or *up* with respect to the surface. Moreover, we compare two approaches of modeling the metalloorganic molecule/metal interface: One with a cluster representation of the metal surface using a localized Gaussian basis set, and one with a slab representation of the surface in conjunction with a periodic cell and a plane wave basis. We compare geometries and binding energies obtained by these two approaches and discuss the difference between them. In addition, we also shed light on the surprising 2-fold symmetry reduction of MPC molecules that has been observed upon adsorption on substrate surfaces in certain cases.^{12,17–19}

II. COMPUTATIONAL METHOD

In this work, we performed first principles calculations using DFT with the generalized gradient approximation (GGA) parametrization by Perdew–Burke–Ernzerhof (PBE) for the XC energy.²⁰ We used two different approaches to represent the SnPc/Ag(111) adsorption system (see Figure 2). In one approach we employ a cluster representation of the surface and use localized Gaussian basis sets. In the other approach, a periodically repeated slab and plane wave basis is used. Henceforth we will call these approaches “cluster” and

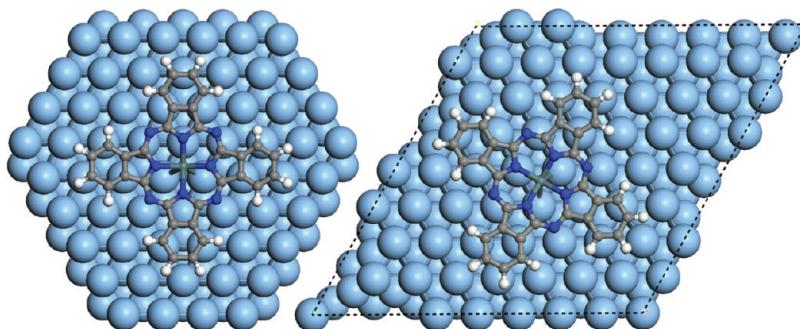


Figure 2. Top view of the cluster and periodic unit cell used in calculations.

"periodic" calculations, respectively. In the cluster calculations each system under study contains 226 atoms: one SnPc molecule ($\text{Sn}-\text{C}_{32}\text{H}_{16}\text{N}_8$) with 57 atoms and an Ag_{169} cluster with three atomic layers. We used two $\text{Ag}(111)$ cluster models. One model has an on-top site in the center on one side and a fcc-hollow site in the center of the flip side. The other model has a hcp-hollow site in the center on both sides. The experimental lattice constant of Ag was used to build the cluster model. To perform cluster calculations we used the resolution of identity (RI) approximation^{21,22} as implemented in the TURBOMOLE v6.1 software package.²³ The basis sets were double- ζ split valence augmented by polarization function DZVP2, for Ag, N, C, and H. For Sn the larger triple- ζ split valence augmented by double polarization function TZVPP2 was used to describe Sn's complex nature of electronic shells. An effective core potential (ECPs) was used to take into account scalar relativistic effects: ECP-28-MWB²⁴ for Ag and ECP-28-MDF for Sn.²⁵ The total number of basis function in the system amounts to 5926. All atoms were allowed to fully relax in the PBE geometry optimizations, which were performed with convergence criteria 10^{-6} Hartree for the energy and 10^{-3} Hartree/Bohr for the gradient.

In the periodic calculations we used the Vienna ab initio simulation package (VASP)^{26–29} using the projector augmented-wave method.^{30,31} In these calculations we have placed the SnPc on the periodically repeated $\text{Ag}(111)$ slab (three layers of Ag) consisting of 192 atoms in the most stable configurations obtained from the cluster calculations and performed geometry optimizations. The calculated lattice constant of Ag is $a_0 = 4.13 \text{ \AA}$, which agrees well with the experimental value of $a_0 = 4.09 \text{ \AA}$.³² The VASP plane-wave basis set energy cutoff was 700 eV, and a Gaussian smearing of 0.1 eV was used for the initial electronic occupations. A thick vacuum level of 20.0 \AA was set up to ensure that there is no spurious interaction between periodically repeated slabs in the normal direction to the surface and the dipole correction was applied. The k -point sampling was performed with (2,2,1) Monkhorst-Pack grids.³³ The structure relaxation was performed within the conjugate-gradient algorithm, using the Hellmann–Feynman theorem for the force calculations. The ionic positions were optimized until the total residual force is less than 0.05 eV/ \AA .

The adsorption energy has been defined as

$$E_{\text{ads}}^{\text{DFT}} = E_{\text{SnPc}/\text{Ag}(111)}^{\text{DFT}} - (E_{\text{Ag}(111)}^{\text{DFT}} + E_{\text{SnPc}}^{\text{DFT}})$$

To account for the missing dispersion effects in the standard implementation of DFT, we describe the vdW forces using the semiempirical approach proposed by Grimme¹⁶ in conjunction with PBE XC-functional (we will call it PBE-D). We performed geometry optimizations with PBE-D starting from the PBE optimized structures but with all Ag atoms kept frozen for both the cluster and the periodic calculations.

III. RESULTS AND DISCUSSION

The key structural parameters for SnPc adsorbed on $\text{Ag}(111)$ have been determined experimentally using the normal-incidence X-ray standing wave technique (NIXSW) and scanning tunneling microscopy (STM).^{4,5,10,11} The SnPc/ $\text{Ag}(111)$ system has also been studied theoretically.^{34–37} In our previous work we have examined adsorption of SnPc on $\text{Ag}(111)$ in the "Sn-down" configuration by means of DFT.³⁵ As far as we know no theoretical studies to date have

considered the impact of vdW forces on the adsorption mechanism, and no detailed investigations of the bonding mechanism of SnPc on $\text{Ag}(111)$ have been reported. In the following we briefly summarize previously published NIXSW and STM results before comparing the results of our DFT and DFT-D calculations with those data.

Stadler et al.^{5,11} carried out careful and comprehensive investigations of the various incommensurate and commensurate phases formed by monolayer (ML) and sub-monolayer coverages of SnPc on $\text{Ag}(111)$. An incommensurate monolayer formed at room temperature, with the SnPc molecules adsorbed in a "Sn-down" geometry with a $\text{Sn}-\text{Ag}(111)$ separation of 2.41 \AA . The Sn atom was found to be located 0.8 \AA below the carbon and nitrogen atoms and they found a significant "back bending" of the benzene rings at the periphery of the Pc ligand toward the surface. For a sub-monolayer (0.68–0.88 ML) film cooled to 150 K, Stadler et al.⁵ found that SnPc assembled in a commensurate phase involving a mixture of "Sn-up" and "Sn-down" molecules. In this phase, assuming that both adsorption geometries were equally probable, Stadler et al.⁵ determined the $\text{Sn}-\text{Ag}(111)$ separation (averaged from the result for two different samples) to be 2.48 \AA for the "Sn-down" molecules and 3.96 \AA for the "Sn-up" configuration. In more recent work, Stadler et al.¹¹ have shown that there can be a significant coverage dependence for SnPc interactions on the $\text{Ag}(111)$ surface. For a coverage of 0.8 ML the $\text{Sn}-\text{Ag}(111)$ distance is 2.23 \AA and 4.08 \AA for the "Sn-down" and "Sn-up" configurations, respectively. The $\text{Pc}-\text{Ag}(111)$ distance at this coverage is found to be 2.92 \AA for both the "Sn-down" and "Sn-up" orientations. In the case of a 1.0 ML coverage, only the "Sn-down" configuration was observed with $\text{Sn}-\text{Ag}(111)$ and $\text{Pc}-\text{Ag}(111)$ separations of 2.25 \AA and 3.09 \AA , respectively. The enlarged $\text{Pc}-\text{Ag}(111)$ distance in this case indicates that different molecular coverages can modify the molecule–substrate interaction. Woolley et al.¹⁰ used a slightly different method of sample preparation — deposition onto a substrate held at 300 °C rather than postdeposition annealing, which led to some subtle differences in the relative ordering of the SnPc molecules. In particular, they observed what they called "a rather counterintuitive" bending of the benzene rings of the molecule away from, rather than toward, the $\text{Ag}(111)$ surface. They nonetheless reproduced (within experimental error) the $\text{Sn}-\text{Ag}(111)$ separation of 2.41 \AA reported in the earlier study by Stadler et al.⁵

Our previous investigations based on DFT calculations for SnPc on $\text{Ag}(111)$ ("Sn-down" configuration only) revealed that SnPc prefers to bind at the hollow binding sites, that is, hcp- or fcc.³⁵ This is due to an optimal overlap of the Sn and the silver orbitals when bound to three silver atoms at the hollow binding sites. Reasonably good agreement with experiment was found for the $\text{Sn}-\text{Ag}$ separation, but the $\text{Pc}-\text{Ag}$ distance was found to be underestimated. These discrepancies between DFT and experiment were assigned to missing dispersion interactions in the calculations.

In order to assess the influence of vdW forces on the molecular and electronic structure and to study the adsorption mechanisms, we discuss our theoretical results separately for the "Sn-down" and "Sn-up" configuration of the SnPc/ $\text{Ag}(111)$ and compare them with available experimental data. We have examined a range of different binding sites (on-top, bridge, hcp-hollow, and fcc-hollow) with different rotational orientations of SnPc and have found binding to the hcp-hollow to be the most stable. We have found small differences between the fcc-hollow

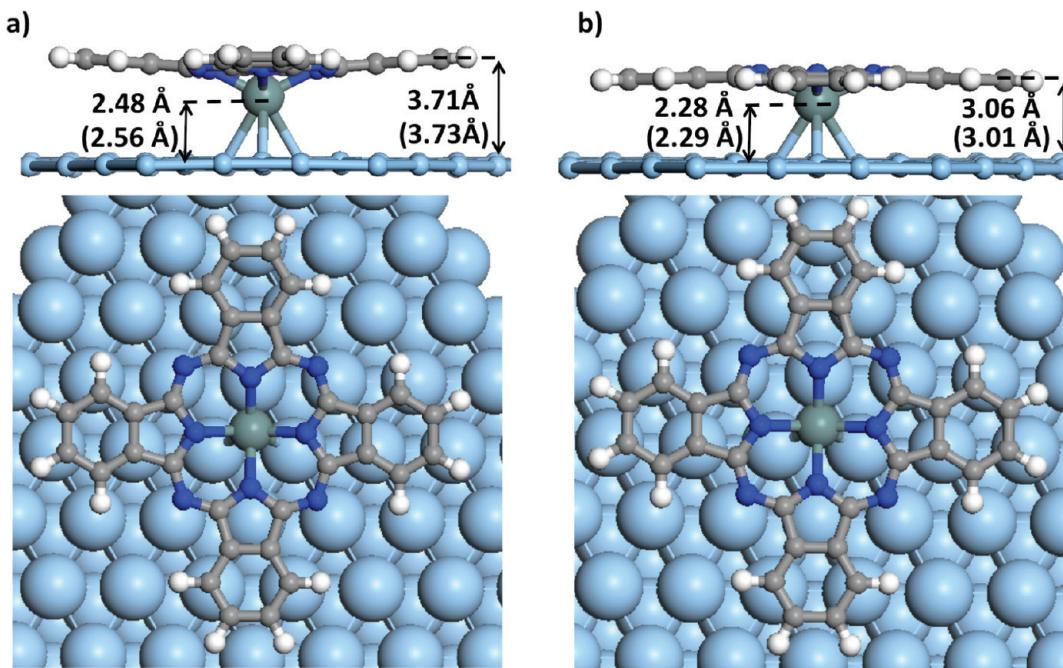


Figure 3. Side and top view of the equilibrium geometries of SnPc/Ag(111) in the “Sn-down” configuration when using (a) standard PBE and (b) PBE-D. Distances in parentheses are obtained from the periodic calculations.

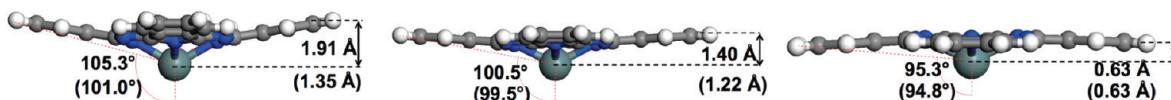


Figure 4. Differences in SnPc geometry after adsorption: (a) free SnPc, (b) SnPc/Ag(111) – PBE, (c) SnPc/Ag(111) – PBE-D. Values in parentheses correspond to the periodic calculations.

and the hcp-hollow site, but choosing either a bridge or on-top adsorption sites as the initial geometry always resulted in migration of the molecule to a nearby hollow site during optimization. For clarity we only report the binding to the most stable hcp-hollow site in this work.

“Sn-down” Configuration. Figure 3 shows a side and top view of the optimized SnPc/Ag(111) interface for the “Sn-down” configuration, using both PBE and PBE-D.

The results of our calculations show that adsorption of SnPc on Ag(111) induces significant distortions in the puckering of the Pc macrocycle, as compared to the free molecule. As can be seen from Figure 3a, the adsorption on Ag(111) as described by PBE shows that the molecule becomes flatter and the molecular plane is almost parallel to the surface. Since the vdw forces are attractive, their inclusion results in further bending of the macrocycle toward the surface (see Figure 3b and cf. Figure 4 below). Table 1 lists the M–Ag(111) and Pc–Ag(111) separation resulting from our cluster and periodic calculations and, for comparison, includes the available experimental data. The separation between macrocycle and the surface is measured as a distance between the average position of the all Ag atoms of the first layer of surface and the average position of the all carbon atoms in accordance with the experiment.³⁵

The Sn–Ag(111) distance predicted by PBE for the “Sn-down” configuration is 2.48 Å (2.56 Å) for the cluster and periodic calculations, respectively, values which are close to, but slightly larger than, the experimentally measured value of 2.25 Å and 2.41 Å by Stadler et al.^{5,11} and the 2.31 ± 0.09 Å value obtained by Woolley et al.¹⁰ PBE-D calculations yield a Sn–

Table 1. Central Metal-Surface M–Ag(111) and Average Macrocycle-Surface Pc–Ag(111) Distances in Å for MPC’s Adsorbed on Ag(111)

	M–Ag					
	cluster		periodic		exp	
	PBE	PBE-D	PBE	PBE-D		
Sn-down	2.48	2.28	2.56	2.29	$2.31(\pm 0.09)^{10}/2.41^{11}$	2.25 ¹¹
Sn-up	5.23	4.33	5.15	4.38	4.08 ¹¹	

	Pc–Ag					
	cluster		periodic		exp	
	PBE	PBE-D	PBE	PBE-D		
Sn-down	3.71	3.06	3.73	3.01	$3.61(\pm 0.16)^{10}/2.92^{11}$	
Sn-up	3.54	3.05	3.74	3.09	2.92 ¹¹	

Ag(111) distance of 2.28 Å (2.29 Å), in good agreement with both of the experiments. The average separation of the Pc macrocycle from the Ag(111) surface as determined by PBE, 3.71 Å (3.73 Å), is in good agreement with that measured by NIXSW by Woolley et al.¹⁰ of 3.61 ± 0.16 Å (albeit with a large experimental error bar) but significantly overestimates that determined by Stadler et al.¹¹ The macrocycle–Ag(111) separation resulting from the PBE-D calculation, 3.06 Å (3.01 Å), is in very good agreement with the NIXSW measurement of 2.92 Å by Stadler et al.¹¹ Moreover, PBE-D calculations reproduce the back bending of the benzene groups of the Pc ligand toward the surface, as observed in the NIXSW experiment.^{5,11}

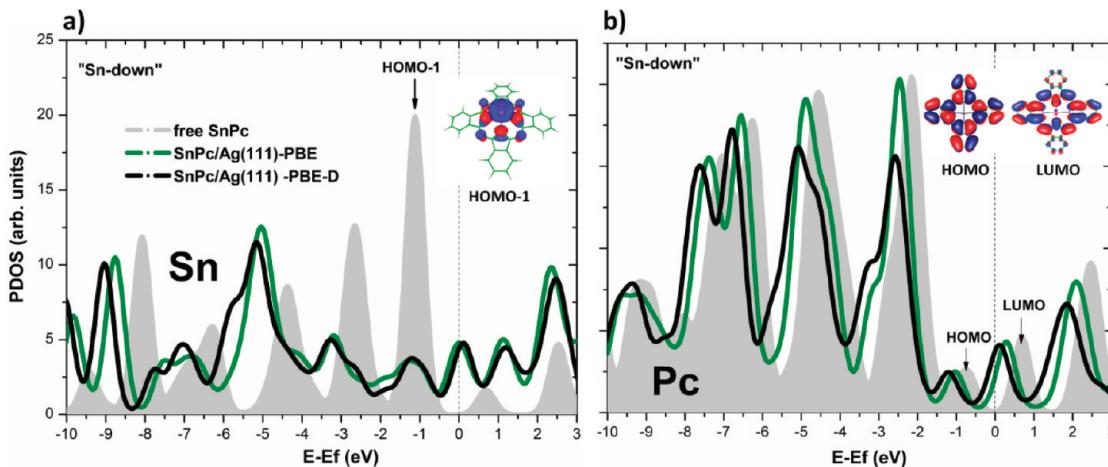


Figure 5. PDOS of Sn (a) and the ligand (b) of SnPc for the free molecule and when adsorbed on Ag(111) in the “Sn-down” configuration, calculated with PBE and PBE-D.

The change of the puckering of the macrocycle upon adsorption on the Ag(111) can be seen in the theoretically determined height of the free and adsorbed molecule and the “shuttle-cock angle” (i.e., the angle between the outermost hydrogens and the central metal atom with respect to the Ag surface normal) (see Figure 4).

The height of the molecule, and the shuttlecock angle as obtained from our cluster calculations for the adsorbed SnPc molecule decrease significantly from 1.40 Å and 100.5° to 0.63 Å and 95° for PBE and PBE-D calculations, respectively, as compared to 1.91 Å and 105.3° for the free SnPc molecule. As shown on Figure 4 the shuttlecock angle and height of the adsorbed SnPc molecule obtained from the periodic calculations are in good agreement the cluster ones in the case of PBE and in excellent agreement for PBE-D. However, there is a significant difference between descriptions of the free SnPc molecule between these two approaches. The free SnPc molecule resulting from periodic calculations appears to be much flatter than in the cluster calculations.

Electronic Structure of the “Sn-down” Configuration.

The modification of the electronic structure of SnPc upon interaction with the surface has been investigated by means of partial density of states (PDOS) plots. For clarity we will compare PDOS's obtained from the cluster calculations only. In Figure 5, we present the PDOS for the free molecule, and for the adsorbed SnPc on the Ag(111) surface in the “Sn-down” configuration, calculated with PBE and PBE-D.

As seen from Figure 5a, upon adsorption the metal atom PDOS changes considerably. This is evidence of strong orbital mixing and charge redistributions between Sn and Ag surface. The two peaks around -1 eV and -2.5 eV disappear and new peaks appear — one at the Fermi level and one around 1 eV (see Figure 5a). The strong mixing shows covalent bonding between Sn and the surface. The disappearance of these Sn-5s peaks could indicate a charge transfer from Sn (HOMO-1) to the surface as has also been suggested based on the experimental data.¹¹ Such a Sn-to-Ag charge transfer would explain the decrease in the Sn–N1 bond length upon adsorption of the molecule. The Sn–N1 bond for the adsorbed SnPc is 2.197 \AA (2.296 \AA for free SnPc), very close to that of 2.146 \AA of the positively charged free SnPc molecule where an electron was subtracted from the HOMO-1.³⁸ The considerable changes in the Sn peaks around E_f as well as in the lower energy

region indicates not only mixing of Sn-5s but also of Sn-4d orbitals with silver sp and d-orbitals.

The electron transfer from the Sn atom to the Ag(111) surface results in a reduction in size of the Sn atom and strong internal redistribution of electrons in the SnPc molecule. This results in changes in the interaction between the Sn and the macrocycle and a flattening of the molecule, as has been previously shown for a positively charged isolated SnPc molecule.³⁸ We note that the change in puckering of the macrocycle of the SnPc molecule adsorbed on the Ag(111) surface in the “Sn-down” configuration reported above for PBE does most probably originate from this suggested charge donation from Sn to the Ag(111) surface, not to the attractive forces between the macrocycle and the surface, which are only treated in the PBE-D calculations. If we examine the PDOS of the Pc part of the molecule (see Figure 5b), we discern that upon adsorption of the molecule on the surface there is a small downshift of the Pc PDOS toward the lower energy region by approximately 0.3 eV . This results in a partial occupation of the SnPc LUMO upon adsorption of the molecule on the surface. Partial occupation of the SnPc LUMO when adsorbed on the Ag(111) has also been found in ultraviolet photoelectron spectroscopy (UPS) experiments by Stadler et al.¹¹ The origin of this partial occupation of the SnPc LUMO is “back-donation” electron transfer from the surface to the Pc macrocycle.

An inclusion of vdW interactions in the calculations does not change the nature of the interaction of the Sn atom with the surface. That is, there is almost no change in the Sn PDOS after adsorption of the SnPc molecule on the Ag(111) surface when calculated with PBE or PBE-D (see Figure 5a). This is expected since the Sn atom makes a covalent bond with the surface and the standard DFT framework does well in describing such interactions. On the other hand, there are considerable changes in the Pc PDOS when dispersion forces are included (see Figure 5b). There is a reduction in size and broadening of the peaks between -2 and -6 eV below the Fermi level. The changes in this energy region indicate stronger interaction of the π -system of the macrocycle with the silver d-bands as compared to PBE results, which is an effect of the decreasing of Pc–Ag separation.

The relatively small changes in the Pc PDOS compared to the Sn PDOS support the view that the adsorption mechanism

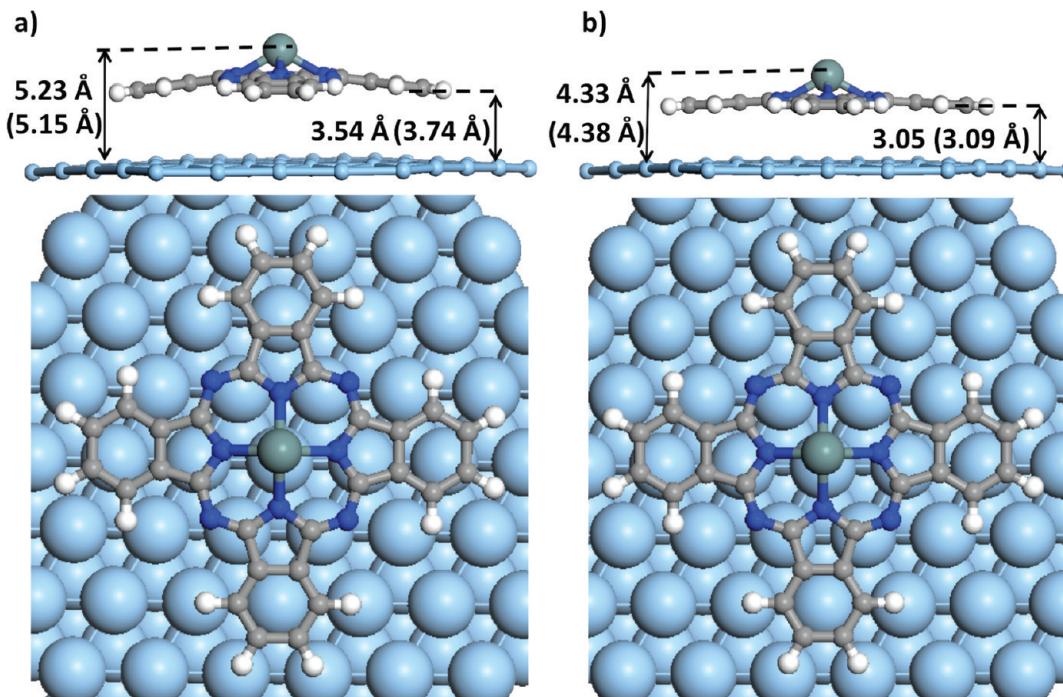


Figure 6. Side and top view of the equilibrium geometries of SnPc/Ag(111) in the “Sn-up” configuration when using (a) standard PBE, (b) PBE-D. Values in parentheses correspond to the periodic calculations.

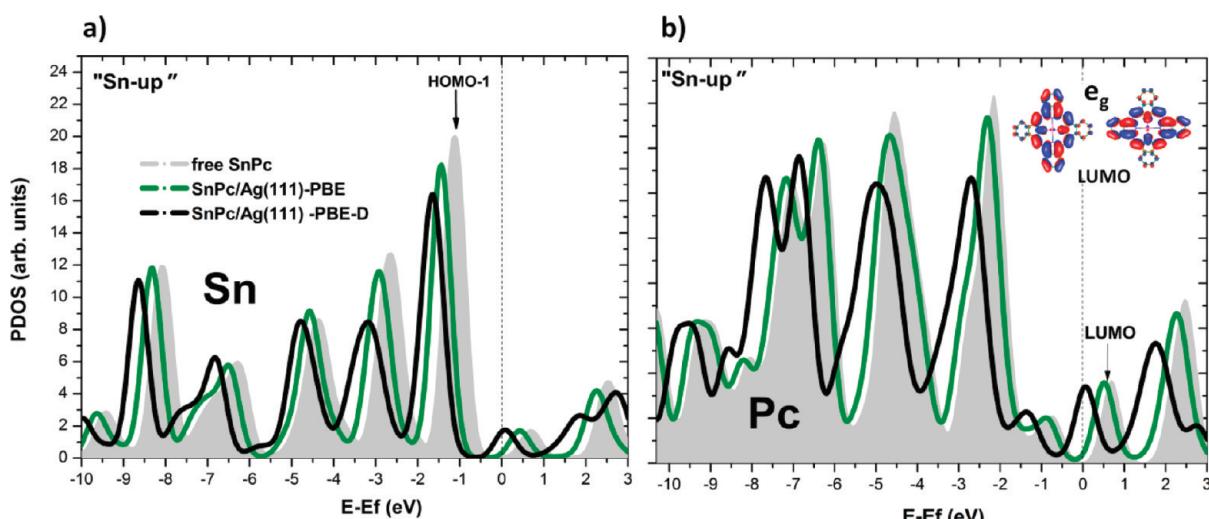


Figure 7. PDOS of Sn (a) and the ligand (b) of SnPc for the free molecule and when adsorbed on Ag(111) in the “Sn-up” configuration, calculated with PBE and PBE-D.

of SnPc on the Ag(111) surface in the “Sn-down” configuration involves a strong interaction of the Sn atoms with the surface (covalent bond), while the interaction between the ligand and surface is weaker (vdW forces).

“Sn-up” Configuration. In the “metal up” configuration, only the Pc macrocycle is interacting with the surface as the distance between the Ag atoms and Sn is too large to be of relevance (see Figure 6). Thus, the Sn–Ag orbital overlap is expected to be negligible compared to the “Sn-down” configuration and the adsorption to be driven mostly by the interactions of the macrocycle with the surface. Figure 6 shows side and top view of the “Sn-up” SnPc/Ag(111) adsorption configuration resulting from PBE and PBE-D calculations obtained from our cluster and periodic calculations.

The PBE calculations yield an equilibrium distance of 5.23 Å (5.15 Å) and 3.54 Å (3.74 Å) for a Sn– and Pc–Ag(111) separation, respectively. Both of these values obtained from cluster and periodic calculations are much longer than NIXSW measured Sn–Ag of 4.08 Å and Pc–Ag of 2.92 Å.¹¹ In addition, the puckering of the SnPc is barely influenced by the adsorption in the PBE calculation, as the molecule more or less retains its gas phase structure (see Figure 6a). This is expected since the interactions of the macrocycle π -system with the surface states are of vdW nature; therefore, standard DFT is not sufficient to model the “Sn-up” configuration of the SnPc/Ag(111) system. Inclusion of vdW forces makes the molecule move closer to the surface and results in significantly flattening of the macrocycle. The PBE-D calculations result in Sn– and

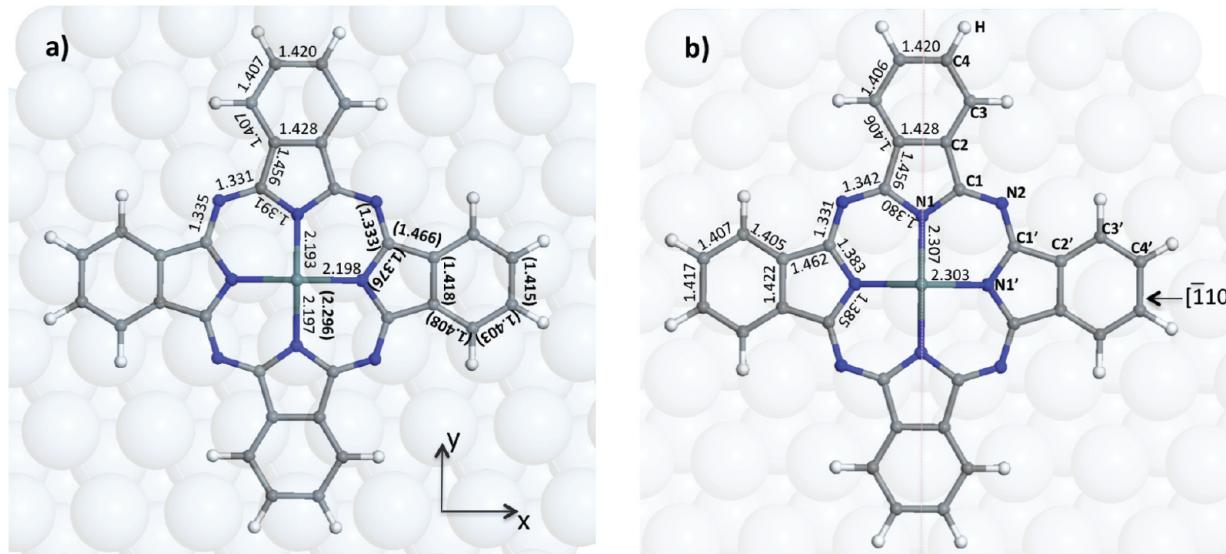


Figure 8. Top view of SnPc adsorbed on Ag(111) in (a) “Sn-down” and (b) “Sn-up” configuration obtained from PBE-D cluster calculations. Only non-equivalent bond distances are shown. The bond distances for free (gas-phase) SnPc are shown in parentheses in (a), and the atomic labels are given in (b).

Pc–Ag distances of 4.33 Å (4.38 Å) and 3.05 Å (3.09 Å), respectively, in very good agreement with the NIXSW values (see Table 1). The height and the “shuttlecock” angle of the SnPc molecule in “Sn-up” configuration from PBE-D calculations is 1.41 Å (1.37 Å) and 100.8° (100.3°), respectively (cf. Figure 4 above). This shows that the puckering of SnPc in the “Sn-up” configuration is less affected by adsorption compared to the “Sn-down” configuration. However, the change in the puckering is considerable also in the “Sn-up” configuration.

Electronic Structure of the “Sn-up” Configuration. Figure 7 shows the PDOS for the “Sn-up” configuration of SnPc/Ag(111) for the Sn and Pc part of the molecule for the free and the adsorbed molecule on the surface calculated with PBE and PBE-D.

Looking first at the Sn PDOS, we discern that there are only minor changes in the position and size of the Sn peaks of the free SnPc molecule upon adsorption on the surface. There is a small shift (~0.2 eV) of the Sn peaks toward the lower energy region together with a slight reduction of their height and some broadening. These effects are slightly enhanced when vdW forces are taken into account (see the peak around -3.1 eV). These minor changes in the Sn PDOS of the free SnPc molecule upon adsorption of the molecule on the surface in the case of the “Sn-up” configuration as compared to the “Sn-down” case show that Sn is not involved in the forming of chemical bonds with the surface in this adsorption configuration.

As mentioned above, the interaction of the macrocycle π -system with the surface states is weak noncovalent, and therefore inclusion of vdW forces in the calculation is expected to have a pronounced effect on the adsorption mechanism. This is indeed reflected in our calculations (see Figure 7b). As has been shown above, PBE significantly underestimates the Pc–Ag separation. This is reflected in the PBE determined PDOS, which lies practically right on top of the free molecule PDOS. This changes when vdW forces are taken into account in the calculations. The most visible changes in the ligand PBE-D PDOS, compared to the free/PBE PDOS, concern the position

and size of the peaks in the energy region from -1.5 to -6 eV below the Fermi level. Upon adsorption, the height of these peaks is reduced and they are broadened, which indicates that the π -system of the molecule is strongly affected by the interaction with the surface, particularly the silver d states. Another subtle but important difference concerns the position of the free molecule lowest unoccupied molecular orbital (LUMO), which is a Pc macrocycle orbital (see inset to Figure 7b). As seen in Figure 7b the LUMO of the free molecule has been partially filled for the PBE-D calculations. We have found that the filling of the free molecule LUMO with electron density from the surface (when vdW forces included) is more pronounced for the “Sn-up” than for the “Sn-down” configuration (c.f. Figures 5b and 7b). This could be explained as the macrocycle faces directly toward the surface in the “Sn-up” configuration, the SnPc LUMO is more accessible for electron donation than in the “Sn-down” case. As vdW interactions are the couplings of the molecule’s and substrate’s electrostatic moments and the resulting induced moments, which is a collective phenomenon occurring at the surface, these interactions are less dependent on the actual adsorption site of the molecule. This is indeed seen in our calculations. The inclusion of vdW forces does not change the horizontal orientation of the SnPc with respect to the surface atoms for the “Sn-down” configuration (see Figure 3b), while in the case of “Sn-up” configuration the SnPc molecule is slightly shifted along the silver row perpendicular to the close packed one (see Figure 6b).

According to the symmetry of SnPc in the gas phase, the molecule should appear in STM images as a “four leave” pattern, or cross. However it has been observed that for some adsorption configurations one pair of aligned aromatic lobes (or spoke of the cross) appears brighter than the perpendicular pair of aromatic lobes.^{12,17} The asymmetry in the brightness has been seen for the adsorption configuration of MPC where one of the pairs of perpendicular aromatic lobes was aligned with one of the closed-packed row of Ag leaving the other pair perpendicular to this close-packed Ag row.^{12,39} This adsorption configuration is very similar to the SnPc configuration on

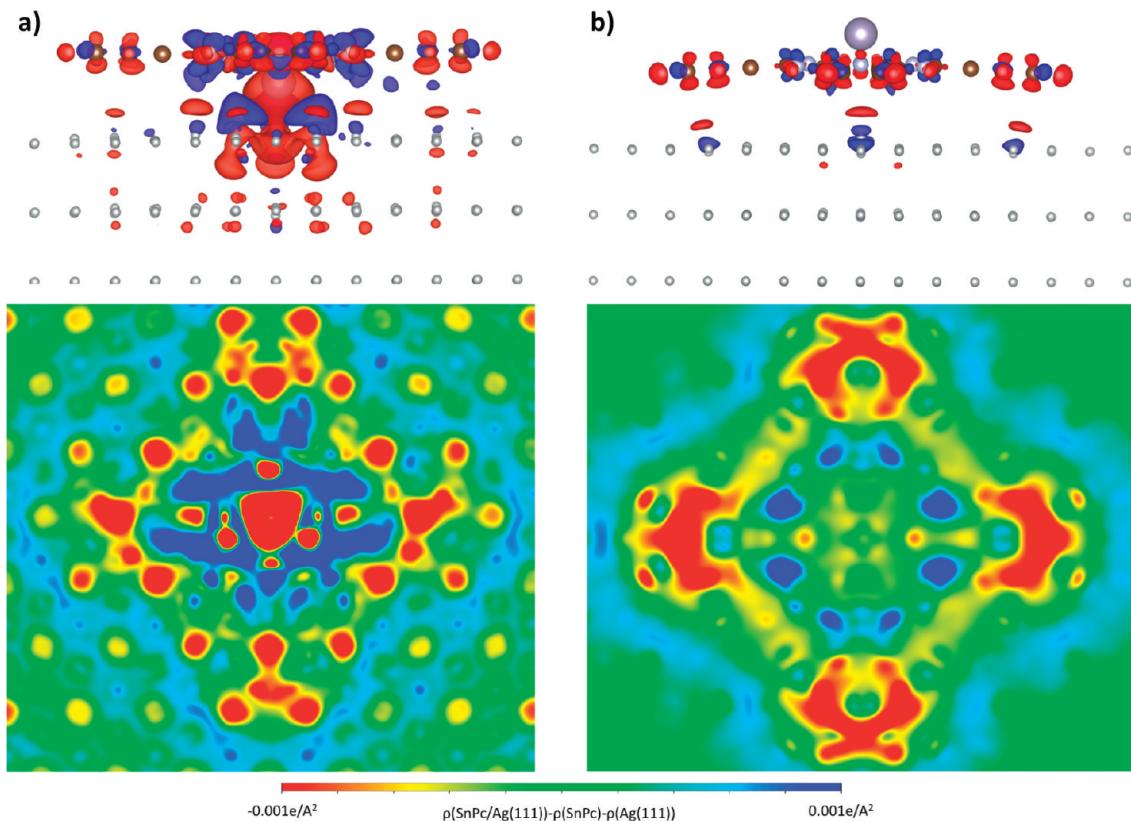


Figure 9. Charge density difference (top) and integrated charge density difference plot into two dimensions (down). (a) for “Sn-down” configuration and (b) “Sn-up”, both obtained with PBE-D. Plots were made with the same value of isosurface 0.001 e/A³. Red (blue) regions correspond to gain (loss) of the charge density in the system upon adsorption of the SnPc on Ag(111). Ag atom sizes are scaled down for clarity. The molecules shown in the bottom of the picture are oriented in the same way with respect to the surface atoms as those in Figure 8.

Ag(111) found theoretically by us in this work for both the “Sn-down” and “Sn-up” cases (see Figure 7). For the former adsorption configuration, the molecule prefers to bind to the hollow binding site which causes a slight vertical shift of the aromatic lobes aligned along the closed packed row of the Ag(111) surface (see Figure 3). This is also seen for “Sn-up” configuration but is less pronounced (see Figure 6). The observed asymmetry in the brightness reduces the symmetry of the STM-images from 4-fold to 2-fold upon adsorption of the molecule on the surface.¹⁷ Such symmetry reduction can be attributed to electronic and/or geometric effects and since STM does not distinguish between these effects the mechanism of it has been unclear. Geometric effects would be, for example, different heights of the two pairs of perpendicular lobes from the surface as the result of buckling, whereas electronic effects would be their different charging. Recently Cuadrado et al.⁴⁰ studied the origin of the 2-fold symmetry reduction for CoPc on Cu(111). Applying the vdW-corrected DFT they conclude that the symmetry reduction has a geometric origin and the different appearance of the perpendicular pairs of lobes in STM is caused by different heights from the surface.⁴⁰ On the other hand, an experimental study by Stadmüller et al.⁴¹ of CuPc on noble metal surfaces reveals electronic rather than geometric origin of the symmetry reduction. They assigned the different appearance of the two pairs of perpendicular aromatic lobes in STM images to the asymmetric charge redistribution in them (at least in the case of certain applied biases).⁴¹

In the following we briefly address the issue of the symmetry reduction from geometric and electronic standpoints for SnPc on the Ag(111) surface. Figure 8 shows the top view of the

SnPc adsorbed in the “Sn-down” and “Sn-up” configuration resulting from PBE-D geometry optimization.

Compared to the free molecular geometry there are some subtle differences in bond lengths for both the “Sn-down” and “Sn-up” adsorption configurations (see Figure 8). The major differences concern the Sn–N1 and C2–C2 bonds. In the “Sn-down” configuration the Sn–N1 bond is shortened, whereas in “Sn-up” it is slightly elongated compared to the free molecule (values given in parentheses in Figure 8a). All other bonds except C1–C2 are elongated upon adsorption of the molecule on the surface for both adsorption configurations when compared to the bond lengths in the free SnPc molecule. There are subtle differences between the bond lengths of these perpendicular pairs of aromatic lobes which are most pronounced for the “Sn-up” configuration (see Figure 8). The C2–C2/C4–C4 bonds are longer than C2’–C2’/C4’–C4’, whereas N1–C1 is shorter than N1’–C1’ (see Figure 8b). Therefore, although in our calculation the symmetry of the molecule is formally reduced from C_{4v} to C_s , when the geometry is scrutinized these small differences in bond length between aromatic lobes pointing in the x and y direction (see Figure 8) give the SnPc in “Sn-up” configuration approximate C_{2v} symmetry, and the “Sn-down” configuration approximate C_{4v} symmetry. It could even be argued that both the “Sn-up” and “Sn-down” configuration has approximate C_{4v} symmetry compared to the level of accuracy of a typical STM measurement. According to our calculations, there are no differences in the height of the perpendicular pairs of aromatic lobes of the SnPc from the surface. Thus, on pure geometrical accounts the deviation from C_{4v} symmetry of SnPc are too

small, and the 2-fold symmetry reduction seen in STM images must have predominantly electronic origin.

The LUMO of the free SnPc is a doubly degenerate e_g symmetric orbital localized on the Pc macrocycle (see inset to Figure 7) and therefore can be filled with up to four electrons. As has been presented above, there is a partial occupation of the states derived from the free molecular LUMO upon adsorption. This leads to splitting of this orbital into two similar nondegenerate MO levels that are localized on different pairs of perpendicular aromatic lobes (see inset to Figure 7), which are in turn not equally populated by electron density due to interaction with the different surface configuration beneath. The different charging of the molecule along different crystallographic axes of the surface is small but can be seen directly in the differences between bond lengths (see Figure 8). Figure 9 shows the charge density difference between the SnPc/Ag(111) system and SnPc and Ag(111) for “Sn-down” and “Sn-up” optimized with PBE-D.

The charge density difference plots molecule shows how complex the interaction of the SnPc is with the underlying silver surface. There is charge density gain on the Sn atom and below it, reaching the second layer of the Ag(111), but depletion in the macrocycle in the region around the central metal atom originating from the pyrrole nitrogens (N1) and C1 (see Figure 8). The charge density difference for the “Sn-up” molecule shows that there are no orbital bonding interactions between Sn and the Ag(111) surface, but we see a similar gain of the electron density on the benzene rings of Pc and depletion on C1 and N1. This charge gain/loss picture is in line with the PDOS and the difference in bond lengths discussed above; that is, there is a strong charge redistribution in the “Sn-down” case due to the interaction of the Sn atom, but for the “Sn-up” case the interaction is only between the macrocycle and the surface. Looking closely at the charge density difference for the “Sn-up” configuration (Figure 9b), one can notice small but visible anisotropy in the charge redistribution along the two perpendicular pairs of aromatic lobes. That is, the charge density of the benzene rings around C4–C4’–C4’ and N1–C1/N1’–C1’ bonds appears slightly different for these perpendicular pairs of lobes,¹² which is also seen in the bond lengths (see Figure 8b).

Adsorption Energies. Table 2 lists the adsorption energies of SnPc on the Ag(111) surface for the “Sn-down” and “Sn-up”

Table 2. Adsorption Energies for the “Sn-down” and “Sn-up” Configuration of SnPc on the Ag(111) Resulting from PBE and PBE-D

	adsorption energy [eV]			
	PBE		PBE-D	
	cluster	periodic	cluster	periodic
Sn-down	-1.35	-0.70	-5.98	-5.28
Sn-up	-0.78	-0.29	-5.65	-4.52

adsorption configurations resulting from our PBE and PBE-D calculations obtained from our cluster and periodic calculations.

Although the resulting adsorption geometries predicted by PBE and PBE-D with the cluster and periodic calculations are in very good agreement, we have found considerable differences between these two approaches in the case of the calculated adsorption energies. As listed in Table 2, adsorption energies obtained from cluster calculations are considerably larger than

equivalent energies obtained from periodic approach for all the systems studied here. For PBE, the difference in adsorption energy between the “Sn-down” and the “Sn-up” case obtained from these two approaches is similar, around 0.5 eV. This is not the case for the PBE-D calculations where “Sn-down” and “Sn-up” cases differ by 0.33 and 0.75 eV for cluster and periodic calculations, respectively. These differences in the adsorption energy between these two approaches originate from a few sources. Cluster calculations are prone to basis set superposition error (BSSE). BSSE is an overestimation of binding energy due to the unequal basis sets between the interacting bonded system and noninteracting separated systems. Lee et al.⁴² have shown that the BSSE is large for the adsorption of the pentacene molecule on the Au(001) surface and that when corrected for the energies obtained by localized orbital basis sets approach the plane wave basis set values. Another source for the discrepancy between the two approaches is the considerable difference in description of the free SnPc molecule between plane-wave and localized Gaussian basis set approach (see Figure 4). Moreover, in the cluster calculations there can be additional spurious interactions between the edge of the cluster and the adsorbed molecule, and in the periodic calculations there can be long-range interactions between molecules in neighboring cells. As far as we know, the adsorption energy of SnPc on Ag(111) has not been determined experimentally; however, the increase in the binding energy from inclusion of vdW forces predicted by PBE-D can be too large to be realistic and is almost certainly overestimated.⁴³ This overestimation comes from the neglect of the screening of dispersive interactions by the bulk of the metal (second and third layer Ag atoms). Therefore, the PBE-D adsorption energy represents an extreme and the real adsorption energy should lie somewhere between 1 and 5 eV. Interestingly, the adsorption geometries are less sensitive to neglect of screening of bulk metal atoms, and our calculations of the SnPc/Ag(111) system employing dispersion corrected DFT in the scheme by Grimme result in very good agreement with experiment in terms of the geometry and electronic structure in the case of the “Sn-up” adsorption configuration and this scheme should be used instead of standard DFT. In the case of “Sn-down” configuration where there is a chemical bond between the Sn and metal surface standard DFT performs reasonably well. Through these simulations we provide another small step to a better understanding of the bonding mechanism of the SnPc molecule on the Ag(111) surface, which should benefit the construction of future experiments and devices based on switching between the “up” and “down” conformation of shuttlecock phthalocyanines on metal substrates.

IV. CONCLUSIONS

By using density functional theory including a semiempirical correction for dispersion interactions, we have investigated the adsorption of a single shuttlecock-shaped SnPc molecule on a Ag(111) surface in two adsorption configurations suggested by experimental studies of this system; that is, with the Sn pointing toward, or away from, the surface. Our calculations show that the bonding mechanism differs significantly for these two adsorption configurations. We find that SnPc in the “Sn-down” configuration binds mostly through the Sn atom and forms covalent bonds with the surface, which leads to strong electron density redistributions in both the molecule and the Ag surface. We show that the standard DFT framework within the PBE approximation yields overall electronic structure and adsorption

geometry in reasonable agreement with experiment for the “Sn-down” configuration. On the contrary, we find that the inclusion of vdW interactions is a prerequisite in order to satisfactorily model SnPc on Ag(111) in the “Sn-up” configuration. Only when vdW forces are included can agreement with experiment be obtained, both in terms of geometry and electronic structure. Within the PBE-D scheme, the molecule flattens and the molecule–substrate separation decreases, which accordingly affects the electronic structure. This is manifested as a shift in the SnPc LUMO toward the Fermi level that results in partial population of this orbital. We have shown that the 2-fold symmetry reduction of the SnPc on Ag(111) seen in STM images should be attributed to electronic, rather than geometric, effects. We explained the mechanism of the symmetry breaking as the molecule interacts with the surface the partial charge transfer to the double degenerate SnPc LUMO lifts its degeneracy and the LUMO splits into two nondegenerate orbitals localized on different pairs of perpendicular aromatic lobes, although the splitting of the LUMO is small in the case of SnPc bound to Ag(111) as computed with PBE and PBE-D. Because of alignment of these pairs of lobes along the silver atom rows with different packing these two new electronic states are not equally populated by electrons from the surface, which appears in STM as pairs of lobes with different brightness.

We have compared two approaches in modeling metalloorganic molecule/metal surface interfaces: one where the surface is represented by a metal cluster and Gaussian type localized basis sets are used, and another one, where a periodically repeated slab represents the surface and plane wave basis sets are used. We have found very good agreement between these two approaches for geometries of the adsorbed species, but differences were found for the description of the free SnPc molecule. Although we have found almost the same energy difference between the “Sn-down” and “Sn-up” configuration obtained from these two approaches, the binding energies obtained from cluster calculations are considerably larger than from periodic ones. Such differences originate from basis set superposition errors in the cluster calculations, the difference in the description of the free molecule between the two approaches, spurious interactions between the edge of cluster and the adsorbed molecule (cluster calculations), and long-range interactions between molecules in neighboring cells (periodic calculations). The empirical dispersion correction gives a large contribution to the adsorption energy for both of these approaches used in this study. However, we suggest that further experimental data regarding the adsorption energy of the system studied here is essential before making a conclusion of the applicability of the semiempirical DFT-D scheme used in this work for predicting binding energies of phthalocyanine molecules on metal surfaces.

ASSOCIATED CONTENT

Supporting Information

Tables of total energies for SnPc/Ag(111); figure of Sn projected density of states onto s, p, d, f orbitals. This information is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +46 (0)31 772 2937. E-mail: jakub.baran@chalmers.se

Notes

The authors declare no competing financial interest.

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