



The role of dispersion forces in metal-supported self-assembled monolayers



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ABSTRACT

The self-assembly of organic molecules (octylamine) is studied by means of periodic DFT calculations including Grimme D2 dispersion scheme. It has been found that in the gas-phase dispersive forces are crucial when *packing* is considered, modifying considerably the potential energy surface compared to the case of a molecular *dimer*. In interaction with a metallic surface (platinum), the electronic interaction between adsorbate and substrate is predominant, dispersion forces mainly increasing the adsorption strength. A detailed study on the structural parameters of the molecule–metal system is reported to gain understanding on the factors affecting their stability. The intermolecular bonding in these systems is analyzed by means of the non-covalent interactions NCI index. The decomposition of the 2D packing along each direction (x, y) highlights the importance of the diagonal contributions in the stabilization of the square pattern. Moreover, the stabilizing nature of H–H interactions between neighboring molecules is supported in this model.

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1. Introduction

The binding of long alkyl chain molecules to metal surfaces is being deeply investigated for application in many technological fields such as films, electronic junctions, tribology or coating [1]. The stability of such systems is mainly due to a competition between metal–molecule and molecule–molecule interactions, whose strength critically determines their physicochemical properties. For instance, in gold/thiol self-assembled monolayers (SAMs), the surface–molecule interaction must be strong to immobilize the alkyl chains on the metal surface [1,2]. Another example is the synthesis of metal nanoparticles in mild conditions, where the alkylamine chains are used as surfactant to stabilize the metallic surface [3,4]. Here, the metal–surface strength must be intermediate: if it is too strong, the molecule blocks the surface site and the particle cannot grow further leading to small nanocrystals, but if it is too weak the particle surface is not stabilized and it grows isotropically leading to large spherical nanoparticles without control on the size or shape. Understanding the nature and the strength of the interactions between surfaces and long chain molecules is

thus of great importance and may help in the design of systems with a specific molecule–surface and molecule–molecule strengths.

The intermolecular interactions in SAMs come from the vicinity of the neighboring molecules that form an ordered two-dimensional layer and are mainly caused by dispersion forces. The role of the dispersion forces between the alkyl chains is poorly understood although it may become crucial in the stabilization of the system. Dispersion forces are commonly estimated from different theoretical approaches. Semi-hybrid functionals have been used to study thiol/gold SAMs [5]. Recently, the implementation of the Grimme approach [6,7] in solid state codes has allowed exploring their role in adsorption systems. It has been found that the inclusion of Grimme DN corrections can significantly affect the calculated geometry of adsorption as well as its strength [8]. Also, the self-assembly of polymers *in vacuo* has been successfully described by using such approach [9]. In the last years, dispersion in short alkyl chains assembly on metals has been studied with *ab initio* methods [10,11]. As regards bonding analysis on SAMs, the reactivity of the tail groups has been studied by conceptual DFT methods [12] and the chemical bond between surfactant and surface studied with the electron localization function ELF [13]. However, little is known about the weak interactions involved in the *packing* of molecules, as in self-assembled monolayers on a solid surface. The aim of the present paper is to highlight the crucial role

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of dispersion forces in the organization of long alkyl molecules in two dimensions. It will be shown that in the gas-phase the energetic profile of a packing of molecules is dramatically affected by such interactions. Standard Density Functional Theory (DFT) calculations are used combined with Grimme D2 approach. A bonding analysis based on Non Covalent Interactions (NCI) index is applied to illustrate the nature of the intermolecular interactions.

2. Models and methods

The platinum (100)-octylamine ($\text{NH}_2\text{C}_8\text{H}_{17}$) system has been chosen because it has been recently reported to lead to stable cubic platinum nanoparticles [3,14]. Such particles are synthesized in mild conditions at the interface between an organic and an aqueous phase. The octylamine is used as surfactant to stabilize the metal particle in the organic (toluene) phase. The particles obtained are cubic and the metal will be modeled by a (100)-terminated five layers-thick slab. The octylamine is investigated in the gas-phase as well as supported on the platinum slab in order to decompose the parameters affecting stability: molecule–molecule distance, molecule packing, surface–molecule distance and coverage.

The calculations are carried out with the revised Perdew Burke Ernzerhof [15,16] functional as implemented in the VASP code [17,18]. Test calculations on the Pt fcc bulk lattice parameter and cohesive energy are shown in Fig. S1, they support the choice of rPBE + D2 level of theory. Projector Augmented Wave (PAW) pseudopotentials [19,20] combined to plane waves (cut-off = 400 eV) represent the electronic distribution. An appropriate set of k -points is used to sample the Brillouin zone. Periodic boundary conditions apply and a vacuum of at least 15 Å is included to avoid interaction between successive layers. Starting from the gas-phase optimized geometry at the rPBE level, calculations are done without geometrical optimization for the gas-phase studies and with the conjugate-gradient algorithm for the surface–molecule interaction studies, with the geometrical constraints specified in each case (see Table S1). The interaction energies are calculated by the formula:

$$A + B = [AB] \quad \text{where } E_{\text{int}} = E_{[AB]} - E_A - E_B$$

thus negative for exothermic reactions.

Dispersion interactions are included by using the Grimme D2 approach as implemented in the VASP code (parameters for Pt: radius = 1.676 Å and $C_6 = 19.46 \text{ Jnm}^6 \text{ mol}^{-1}$ obtained from [7]). As noticed in the literature [8], the problem of metal screening of dispersive forces can be roughly corrected by including dispersion only on the uppermost slab layer. We have considered this possibility together with the pure rPBE and full D2, denoted as 1L, rPBE and D2 respectively. Tests on the propylamine dimer potential energy curve have been carried out at the MP2/6-311++g(3df,2pd), BSSE corrected, together with the rPBE and rPBE + D2 levels, and show very good agreement with the rPBE + D2 setting used in the present work, as can be seen in Fig. S2.

It has been recently shown that although the energetic balance at weak interactions is cumbersome to detect from energetics, the density (ρ) reconstruction by those methods is accurate enough to reveal the interactions present in the system. This is the principle lying behind the recently reported index for detecting non-covalent-interactions, NCI [21]. This index enables the identification and characterization of weak interactions of various strengths as chemically intuitive reduced density gradient isosurfaces that reveal both stabilizing (hydrogen bonds, van der Waals) and destabilizing (steric clashes) interactions. It can also be applied to ionic interactions [22]. In order to achieve a better comprehension of the nature of bonding and packing, representative systems will be

studied by means of the NCI method. The NCI analysis has been carried out with the critic2 code [23] and visualized in VMD [24].

3. Results and discussion

We have chosen to investigate independently the key factors in the stabilization of the system surface–molecule so we can derive the nature and the strength of the forces responsible for each interaction. Thus, we have computed the gas-phase molecule–molecule interaction as regards their interatomic distance, the relative orientation and the packing effect. Then, we have studied the surface–molecule interaction concerning the adsorption site, the distance surface–molecule, the tilting angle and the coverage.

3.1. The molecule–molecule interaction in the gas-phase

The potential energy surface of an octylamine dimer in the gas-phase is presented in Fig. 1. It can be seen that the curve decays asymptotically and reaches a minimum for a distance of 5.5 Å (rPBE) and 5.0 Å (D2). The energy gain with respect to the isolated molecule in the gas-phase is almost athermic for rPBE and only slightly exothermic, -0.12 eV , for D2. Compared to the propylamine results (Fig. S2), the energy gain is of 0.05 eV . Such gain is due to the longest alkyl chain that increases the dispersive interactions.

The packing effect of the molecule on the surface has been calculated by considering the molecule in a tetragonal unit cell repeated in three dimensions. The a parameter is modified so as to consider the distance between consecutive neighboring molecules. The curves obtained, presented in Fig. 1, show a behavior similar to that of the dimer for the pure rPBE functional. Instead, a qualitative change is observed for the D2 calculations: a minimum in the curve appears at a distance of 4.5 Å, with an energy gain of -0.28 eV . Therefore, dispersion forces seem to be crucial for representing packing in two-dimensions in the gas-phase.

3.2. Molecule-surface interaction

The adsorption site preferred for the $\text{NH}_2\text{C}_8\text{H}_{17}$ molecule is a quasi-top site [14], as found also for NH_3 [25]. Concerning the molecule orientation on the surface, previous calculations on Au/thiol SAMs show that the alkyl chains are not perpendicular to the surface but tilted [26–28], and is also the case in Ag/thiol systems [29]. Our calculated value for the tilting angle α (see Fig. 2) is $\sim 23 \text{ deg}$ (rPBE), $\sim 27 \text{ deg}$ (D2) with a gain in energy of -0.33 eV (rPBE) -0.55 eV (D2) with respect to the molecule perpendicular to the slab. Also, the relative orientation of the molecule with respect to the surface sites has been explored through the radial angle β , 45 deg being the optimal angle for all the methods (see Fig. 2). The system is much less sensitive to this radial angle than to the tilting angle, the gain in energy is small (0.09 eV for rPBE, 0.05 eV for rPBE + D2).

The coverage effect has been investigated for coverage values θ from 0.11 to 0.5. The coverage is defined as the number of molecules per surface Pt atom as in Table 1. For all the coverages considered the adsorption occurs on a quasi-top position, the platinum atom to which the amine is bonded slightly moving upwards. The most favorable adsorption energy is found for $\theta = 0.125$, and becomes less favorable as the coverage increases. For a coverage of $\theta = 0.5$ the amine is almost vertical to the surface, but as the coverage decreases the tilting angle increases reaching values around 30 deg. This is an indication of the higher intermolecular interaction occurring when the molecules are close to each other (high coverage). Low coverage involves almost exclusively

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