Adsorption and dissociation of iron phthalocyanine on H/Si(111): Impact of van-der-Waals interactions and perspectives for subsurface doping

Benjamin Geisler and Peter Kratzer

Fakultät für Physik, Universität Duisburg-Essen and Center for Nanointegration (CENIDE), Campus Duisburg, Lotharstr. 1, 47048 Duisburg, Germany
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The adsorption of iron phthalocyanine (FePc) on the passivated H/Si(111) surface is explored from first principles. We find that the organic molecule is predominantly physisorbed with a distance to the surface of $2.6 \pm 0.1$ Å, but also exhibits sizable resonance with the underlying substrate. This establishes the present system as interesting mixed covalent-van-der-Waals-bound test case, which we use to compare the impact of different approaches to van-der-Waals interactions. (Spin-polarized) scanning tunneling microscopy (SP STM) images are simulated, selectively accessing different molecular orbitals via the applied bias voltage in the spirit of scanning tunneling spectroscopy. Comparison with experimental STM images reveals very good agreement. We find a significant magnetic contrast exceeding $\pm 1$ Å in the SP STM images for $-2$ and $+1.5$ V. Binding energies of different (transition metal) atoms in the center of the Pc ring are presented, which particularly show that Fe is strongly bound in the molecule (about 9.6 eV). Finally, we discuss different reactions for subsurface doping by room-temperature FePc deposition and point out two feasible reactions.

INTRODUCTION

The exploration of viable routes towards Si-based spintronics devices [1] is of key importance, owing to the abundance of Si and its unmatched role in modern semiconductor technology. Magnetic functionalization of Si by a controlled doping with transition metal (TM) impurities is a potential strategy. Despite intense research, comprising recent studies of formation energies and magnetic properties of isolated TM impurities and impurity pairs [2], the dependence of magnetism on the doping concentration [3, 4], or Mn $\delta$ doping of Si [5–7], at present Mn-doped GaAs dominates the field [8–10].

For a rational materials design, it is crucial to improve the fundamental understanding of the interaction mechanisms between impurities and the surrounding host matrix. We recently promoted (spin-polarized) scanning tunneling microscopy (SP STM) [11] as a powerful method to explore bulklike interaction properties of impurities in semiconductors on the atomic scale by exploiting passivated surfaces [12]. Specifically, we focused on TM impurities below the H/Si(111) surface. The passivating H layer could be added after growth and subsequent cleavage of a sample; however, exposing the doped system to a wet-chemical treatment [13] will cause strong reactions of the TM impurities with H. Hence, a strategy to achieve a controlled subsurface doping of the H/Si(111) system after preparation would be valuable. It was claimed recently that this can be accomplished by the adsorption of iron phthalocyanine (FePc) on the H/Si(111) surface [13]. This is particularly compelling owing to the fact that Fe is one of the fundamentally most interesting impurities in Si, since its magnetic moment could not be unambiguously determined from first principles so far [12].

The study of surface reactions in hybrid inorganic-organic systems is a rich topic of its own. Considerable research focuses on the adsorption of molecules on metallic [14–16], semiconducting [17–19], or insulating [20] surfaces, magnetic properties of TM-based molecules and their interactions with ferro- and nonmagnetic substrates [21, 22], and magnetic switching phenomena [23], which aim at spin-dependent molecular electronics [24, 25]. The Kondo effect can be observed in magnetic molecules deposited on metal surfaces [26, 27]. Given that the impact of the surface on the electronic structure of the adsorbate is minute, these systems are also attractive models to gain fundamental insight by comparing experimental and time-dependent density functional theory (TDDFT) results, for instance, on optical properties of Pc-derived molecules [28]. Naturally, van-der-Waals (vdW) interactions are of central relevance in this field.

Here we explore the adsorption of FePc on H/Si(111) from first principles. We find that the organic molecule is predominantly physisorbed, but also shows significant resonance with the underlying substrate. We use this paradigmatic case of a system in a mixed covalent-vdW-bonding state to compare the impact of different established [29, 30] and recent [31, 32] approaches to vdW interactions. (SP) STM images are simulated, selectively accessing different molecular orbitals via the applied bias voltage in the spirit of scanning tunneling spectroscopy, and compared to experiment. The SP STM images exhibit a magnetic contrast that exceeds $\pm 1$ Å for $-2$ and $+1.5$ V. Binding energies of different (TM) atoms in the center of the Pc ring are presented, which particularly show that Fe is strongly bound in the molecule (about 9.6 eV). Finally, we discuss different mechanisms for subsurface doping involving room-temperature FePc deposition and point out two feasible reactions.

METHODOLOGY

We performed spin-polarized density functional theory [33] (DFT) calculations within the plane-wave and ultrasoft pseudopotential (PP) framework as implemented in the Quantum Espresso code [34, 35] and compare to results obtained with the full-potential, all-electron (AE) FHI-aims code [36] which
Figure 1. Adsorption of a single FePc molecule on the H/Si(111) surface. (a) Adsorption energies $E_{\text{Ads}}$ as functions of the molecule-surface distance, comparing different vdW methods. The inset compares three distinct adsorption sites. (b) Optimized gas-phase FePc geometry and corresponding spin density. (c) 3D, (d) side, and (e) top view of an FePc molecule adsorbed at a H/Si distance, comparing different vdW methods. The inset compares three distinct adsorption sites. (b) Optimized gas-phase FePc geometry and corresponding spin density. (c) 3D, (d) side, and (e) top view of an FePc molecule adsorbed at a H/Si(111) A site as obtained within the PBE+PP+D2 framework ($U_{\text{fc}} = 3$ eV). The spin densities exhibit a polarized H-Si bond below the Fe ion (blue/red corresponding to positive/negative).

The DFT treatment of FePc is nontrivial due to numerical instabilities. Calculations employing the PBE exchange-correlation functional often lead to a symmetry-broken $D_{2h}$ ground state, whereas hybrid functionals such as B3LYP preserve the $D_{4h}$ symmetry of the molecule [51]. We used the B3LYP electronic structure as reference, which we found to be qualitatively reproduced by PBE+$U$ [52] with a small $U_{\text{fc}} = 3$ eV, as is has also been utilized in the literature [15, 53]. In order to obtain unbiased binding energies, we did not apply a Hubbard $U$ in those cases, assuring carefully that the symmetry is not broken.

Table I. Optimized distances and adsorption energies as obtained by different vdW approaches for a single FePc molecule adsorbed on the H/Si(111) surface at site A (cf. Fig. 1).

| Method   | PP   | D2  | D3  | TS  | +TS   | +MBD |
|----------|------|-----|-----|-----|-------|------|
| Distance (Å) | 5.2  | 4.8 | 4.5 | 4.8 | 6.1  | 5.8  |
| $E_{\text{Ads}}$ (eV) | 0.18 | 1.45 | 1.5 | 2.2 | 2.27 | 1.65 |

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The adsorption energy curves exhibit a typical potential shape, diverging for small distances and approaching zero (corresponding to the total energy sum of separated systems) from below for large distances. Three distinct adsorption sites are compared: centering Fe above the first Si layer positions, i.e., above one of the H atoms (A), above the second/third Si layer positions (B), and above the fourth Si layer positions (C), which correspond to the hollow centers of the topmost bilayer rings [Fig. 1(e)]. The curves have been obtained from rigid atomic structures, i.e., no relaxation beyond the individual equilibrium geometries of molecule and surface has been performed. Successive calculations optimizing all atomic positions at the adsorption distance have shown that adsorption at site A is most stable [Fig. 1(a)]. Energy differences with respect to sites B and C amount to only a few meV; the same applies to different rotation angles of the molecule. Thus, we conclude that FePc is highly mobile on the H/Si(111) surface.

The resulting adsorption energies and distances are summarized in Table I. Interestingly, already PBE without further vdW corrections provides a shallow adsorption minimum of \( \sim 0.18 \text{ eV} \) near 3.2 Å despite the chemical inertness \([54]\) of the H/Si(111) surface. However, this adsorption energy is certainly far too low, and the equilibrium molecule-surface distance will be severely overestimated. Indeed, we find that FePc attaches more closely to the substrate if vdW interactions are taken into account; all considered vdW methods provide adsorption distances within an interval of 2.6 ± 0.1 Å. The adsorption energies are more strongly spread: Predictions based on the D2, D3, and MBD approaches range from 1.45 to 1.65 eV, whereas the TS method results in a much stronger binding of about 2.2 to 2.27 eV. Thus, a many-body treatment of the vdW interactions \([32]\) corroborates the results of D2 (and D3). Interestingly, we find very good agreement for two distinct implementations (PP vs. AE) of the TS method in two individual codes [Fig. 1(a)].

The results shown in Fig. 1(a) and Table I can be compared to other hybrid inorganic-organic systems. For 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) on Ag(111) \([16]\), PBE provides a shallow adsorption minimum of about 0.3 eV at a distance \( \sim 1 \text{ Å} \) larger than the experimental value. Inclusion of D2 vdW corrections severely overestimates the adsorption energy by \( \sim 1 \text{ eV} \) (40%), simultaneously providing an almost correct molecule-surface distance. In that case, screening effects of the metal substrate play an important role, and the performance of D2 will be significantly better for the present system. For anthracene and pentacene on Ag(111) \([14]\), PBE predicts a shallow adsorption minimum of \( \sim 0.1 \text{ eV} \), and the surface-molecule distance is lowered by about 1 Å after inclusion of vdW interactions. The adsorption energy obtained with the MBD approach is in almost perfect agreement with the experimental value.

The \( D_{dz^2} \) environment of the Fe\(^{2+} \) ion results in a FePc magnetic moment of 2 \( \mu_B \) as expected from ligand field theory. Its spin density is shown in Fig. 1(b). The adsorbed molecule retains its gas-phase magnetic moment for all methodologies considered here, and it becomes obvious from Figs. 1(c)-(e) that also the shape of the spin density is largely preserved, apart from a slight compression of the lobe directed towards the substrate. Interestingly, we observe a sizeable spin polarization of the H-Si bond in the substrate below the Fe ion.

At first sight, it appears that the proximity of the surface has...
only modest impact on the electronic structure of the molecule [Fig. 2(a)], which is different e.g. for anthracene and pentacene on Ag(111) [14]. Relative to gas-phase FePc, the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is almost unaffected. Both reside within the valence band or the conduction band of the substrate, respectively. A finite density of states emerges at $-3.5$ eV. Specifically, the Fe 3$d_{x^2-y^2}$ states are strongly broadened; while the occupied majority-spin state at $-3$ eV shifts to $-2.8$ eV, its unoccupied equivalent in the minority-spin channel retains its position. The H 1$s$ and Si 2$p$ states below the Fe ion clearly respond to the presence of the molecule as well, reflecting the induced spin polarization and exhibiting an Fe-3$d_{x^2-y^2}$-H-1$s$-Si-2$p$ resonance [Fig. 2(a)]. Close inspection of the atomic positions reveals that Fe and H leave their respective planes and reduce their distance by 0.05 Å. This attractive interaction shows that the system enters a mixed covalent-vdW-bonding state, which exemplifies that the inclusion of vdW interactions does not only quantitatively improve the results, but is of qualitative importance for a proper modeling of FePc adsorption on H/Si(111). Hence, this system emerges as interesting test case for different vdW corrections in the field of electronic structure theory [29–32, 55].

Figure 2(b) shows simulated STM and SP STM images for an adsorbed single FePc molecule on the H/Si(111) surface at site A, together with a line scan for different bias voltages [Fig. 2(c)]. For the filled-state images ($V < 0$), the H sites of the substrate can be identified by white spots [12]. The $D_{4h}$ symmetry of the molecule is clearly reflected in all panels. The distinct lobes that can be seen for $-1.2$ V (cross-like shape) merge for voltages of higher magnitude (flower-like shape), consistent with experiment [18]. Moreover, while for $-1.2$ V the outer parts of the lobes are dominant, a feature appears in the center of the molecule with increasing bias voltage that can be clearly seen from the line scans and is also observed experimentally [18]. In our simulations, the molecule is detected $\sim 4$-5 Å above its physical position and $\sim 3$-4 Å above the substrate-related background, with an apparent diameter of $21 \pm 1$ Å (structurally 15 Å). Experimentally, its signature appears a little larger, exhibiting a height of $\sim 5$ Å above the substrate-related background and a diameter of $\sim 25$ Å at $-2.25$ to $-2.65$ V and 10-20 pA [18]. Overall, the agreement between simulations and experiment is very good.

We find that the SP STM magnetic contrast is significant, exceeding $\pm 1$ Å for $-2$ and $+1.5$ V. Since SP STM does not correspond to a mapping of the spin density (Fig. 1), but of the states near the Fermi energy, we see a negative response for $-1.2$ V (red, largest at the outer lobe parts) that switches to a positive signal for $-2$ V (blue, largest between the lobes). Finally, inclusion of the majority-spin Fe 3$d_{x^2-y^2}$ state for a bias voltage of $-3.5$ V leads to a positive feature in the center. In turn, this feature appears negative and even more pronounced for a mapping of the unoccupied states beyond $+2$ V (not shown).

### BOUNDING ENERGIES OF TRANSITION METAL IONS IN Pc MOLECULES

We now explore energetic aspects of different gas-phase Pc molecules, particularly FePc, and the influence of the exchange-correlation functional. Figure 3 shows optimized atomic structures of different Pc molecules. The corresponding binding energies of different central atoms in an empty Pc ring are given in Table II. They are defined as

$$E_{\text{Bind}} = E_{\text{Molecule}} - E_{\text{Empty Pc ring}} - \sum_i \Delta N_i E_{\text{Atom}}^i,$$

where the first two terms are the total energies of the molecule and the empty Pc ring as reference, $\Delta N_i$ is the difference of atoms of species $i$ between molecule and reference, and $E_{\text{Atom}}^i$ denotes the total energy of an isolated atom of species $i$. Two H atoms are bound twice as strong in the Pc ring (9.22 eV) as in a H$_2$ molecule (PBE: 4.45 eV), while four bound H

| Atom | $E_{\text{Bind}}$ (eV) | $m$ ($\mu_0$) |
|------|-----------------|--------------|
| Ti   | 10.87           | 2            |
| Cr   | 9.52            | 4            |
| Mn   | 9.11            | 3            |
| Fe   | 9.59            | 2            |
| Co   | 9.96            | 1            |
| Cu   | 7.69            | 1            |

### Table II. Binding energies and magnetic moments of different central atoms in an empty Pc ring, calculated within PBE+PP. 2H, 4H, Fe + 2H, and Si + 2H correspond to (a), (b), (d), and (f) in Fig. 3, whereas Fe and Si correspond to (c) and (e), respectively.
atoms are less favorable than the former case plus an isolated H₂ molecule. We find that Fe is even more strongly bound (9.59 eV), as are most of the other studied TM atoms, particularly Ti. A Si atom in a Pc ring is bound with 8.51 eV, which is almost twice as high as in Si bulk (PBE: 4.6 eV). Both FePc and SiPc can bind two additional H atoms above and below the molecular plane. While in the case of FePc the formation of an isolated H₂ molecule is energetically favored, SiPc-2H is stable against decomposition with an energy gain of 1.61 eV.

In addition to the binding energies, Table II also lists the spin magnetic moments of different molecules. The values for the more common types such as MnPc, FePc, CoPc, or CuPc are well known [26, 53]. We also find (high) magnetic moments for TiPc and, particularly, CrPc. Most peculiarly, we observe a very stable magnetic moment of 2 μB for SiPc, the spin density extending over the entire molecule [Fig. 3(e)], while that of FePc is confined to the center.

In order to validate the very high binding energies we obtained for TM-Pc molecules, Table III compares results calculated with different exchange-correlation functionals for FePc and a Pc ring with two H atoms [Fig. 3(a)]. In particular, hybrid functionals like B3LYP, PBE0, or HSE06 are commonly used for organic molecules [56–58]. The PBE results obtained within the PP and AE frameworks are in excellent agreement. LDA shows the well-known overbinding. For FePc, the binding energies provided by the hybrid functionals are roughly 1 eV smaller than the PBE results, but still very high. For the Pc ring with two H atoms, hybrid functional results are similar to PBE. Hartree-Fock calculations lead to significantly smaller binding energies for both systems, but since they ignore all correlation effects, their appropriateness for larger organic molecules can be questioned. The magnetic moment of FePc is 2 μB in all cases. While Fe is more strongly bound than two H atoms in LDA and PBE, the reversed prediction is made by hybrid functionals and Hartree-Fock. HSE06 and PBE0 provide very similar results, which shows that the screening of the Coulomb interaction in HSE06 is irrelevant on the present length scale. We conclude that the very high binding energies obtained by PBE are indeed reasonable.

### Table III. Binding energies |Efinal| (eV) of a central Fe atom or two H atoms in FePc and Pc, respectively, calculated with different exchange-correlation functionals and Hartree-Fock (HF). For PBE, benchmarking with AE results underlines the reliability of the PP method.

|        | PP      | AE      | LDA | B3LYP | PBE0 | HSE06 | HF  |
|--------|---------|---------|-----|-------|------|-------|-----|
| Fe in FePc | 9.59    | 9.57    | 11.74 | 8.23  | 8.69 | 8.72  | 5.81 |
| 2H in Pc  | 9.22    | 9.24    | 10.59 | 9.15  | 9.24 | 9.27  | 6.27 |

### Table IV. Different reactions for the injection of isolated interstitial or substitutional Fe impurities into the H/Si(111) subsurface layers [cf. Fig. 4] from FePc and FePc-2H. ∆E is the DFT total energy difference between the final and the initial state; a negative value indicates that the final configuration is preferred.

| Reaction | ∆E (eV) |
|----------|---------|
| FePc + pure H/Si(111) → Fe subs. + SiPc | +2.79 |
| Fe subs. + SiPc-2H + 2× H-Si bond broken | +3.51 |
| Fe subs. complex with Si self-inter. + empty Pc ring | +8.60 |
| Fe subs. + Si self-inter. + empty Pc ring | +10.73 |
| Fe inter. + empty Pc ring | +6.15 |
| Fe inter. + Pc + 2× H-Si bond broken | +3.70 |
| FePc-2H + pure H/Si(111) → Fe subs. + SiPc-2H | −0.60 |
| Fe subs. complex with Si self-inter. + Pc | +2.05 |
| Fe inter. + Pc | −0.40 |

**SUBSURFACE DOPING**

It has been recently proposed on the basis of STM imaging that subsurface doping can be achieved by room-temperature deposition of FePc on H/Si(111) [13]. Tables II and III show that Fe is very strongly bound to the organic part of the molecule and thus quite difficult to extract. This raises the question whether the suggested doping strategy is realistic, particularly since a combined experimental-theoretical analysis of the STM observations remained inconclusive [12, 13].

In a first step towards addressing this complex question, DFT total energy differences ∆E = Efinal − Einitial of several distinct reactions (Table IV) can be considered under the constraint that the number of atoms of each species has to be conserved. Positive ∆E indicates an endothermic reaction. For instance, the Fe atom could leave the FePc molecule and replace a Si atom in the host (substitutional Fe); subsequently, the Si atom is incorporated in the rest of the molecule, forming SiPc in which the Si atom is more strongly bound than in bulk Si, as discussed above, leading to ∆E = +2.79 eV for this scenario. Additionally, two H atoms could leave the passivating H layer and adsorb on the SiPc molecule [Fig. 3(f)]. The defect energy associated with a missing H atom can be approximated by the H-Si binding energy (PBE: 3.39 eV, ∆E = +3.51 eV). A third possibility is the formation of a Si self-interstitial impurity, which can either form a complex with the substitutional Fe impurity or be isolated from it. One can see from Table IV that all scenarios based on a removal of Fe from FePc with subsequent implantation into the H/Si(111) matrix are energetically highly unfavorable, even when compared to typical room-temperature energies (25 meV) and irrespective of the final Fe site, i.e., interstitial or substitutional. The situation remains unchanged if one tentatively lowers the PBE binding energy of FePc to a hybrid functional result (Table III). In addition to the total energies of different initial and final states, kinetic barriers caused by transition states might inhibit the Fe exchange process.
The origin of the highly positive values of $\Delta E$ lies in the stability of the initial state, but also in the unfavorable final states considered so far. Let us now assume that two H atoms adsorb on a gas-phase FePc molecule [Figs. 3(d) and 4(a)]. If the Fe atom occupies a substitutional site after the reaction [Fig. 4(c)], the removed Si atom can be incorporated in the Pc ring, which results in SiPc with two additional H atoms above and below the molecular plane (SiPc-2H), which is very stable (Table II). This scenario optimizes both $E_{\text{Initial}}$ and $E_{\text{Final}}$ and leads to $\Delta E < 0$. If the Fe atom is integrated on an interstitial site [Fig. 4(d)], not SiPc-2H, but simply Pc remains after the reaction, resulting in $\Delta E < 0$ as well.

Hence, the latter two mechanisms are statistically relevant (neglecting kinetic barriers). The crucial point is the adsorption of H atoms on the FePc molecule prior to the reaction at the H/Si(111) surface. This can occur if, in addition to the FePc molecules, H atoms are evaporated from the crucible in the experiment, or if excess H atoms exist in the vicinity of the passivated surface. Moreover, a destabilization of FePc due to interactions with the H atoms in the passivating layer, as discussed above, facilitates the process.

We conclude from this analysis that subsurface doping of H/Si(111) by room-temperature deposition of FePc molecules is possible, but the probability of the necessary steps in the reaction is low due to strongly bound Fe ion in FePc. More detailed investigations should be done in this field.

**SUMMARY**

We studied the adsorption of iron phthalocyanine (FePc) on the passivated H/Si(111) surface from first principles. According to our findings, the organic molecule is predominantly physisorbed with a distance to the surface of 2.6 ± 0.1 Å, but also shows significant resonance with the underlying substrate. We used this paradigmatic case of a system in a mixed covalent-van-der-Waals-bonding state to compare the impact of different approaches to van-der-Waals interactions. (Spin-polarized) scanning tunneling microscopy (SP STM) images were simulated, selectively accessing different molecular orbitals via the applied bias voltage, similar to scanning tunneling spectroscopy. Comparison with experimental STM images revealed very good agreement. We found a considerable magnetic contrast exceeding ±1 Å in the SP STM images for −2 and +1.5 V. Binding energies of different (transition metal) atoms in the center of the Pc ring were presented, showing in particular that Fe is strongly bound in the molecule (about 9.6 eV). Finally, we discussed different mechanisms for subsurface doping by room-temperature FePc deposition and pointed out two feasible reactions.

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