

Physisorption of benzene on a tin dioxide surface: van der Waals interaction

Matti Viitala, Mikael Kuisma, and Tapio T. Rantala

Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland

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An adsorption study of the benzene molecule on SnO_2 (110) surfaces with the density functional theory is extended to include the van der Waals interaction. We compare adsorption onto two model surfaces of SnO_2 , oxygen rich (stoichiometric) and oxygen poor (reduced), considered as limiting cases of varying oxygen abundance. With the chosen van der Waals approach [M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004)] it is found that on the stoichiometric surface, where binding has both a covalent nature and an ionic nature, with the addition of the van der Waals interaction the adsorption energy becomes somewhat stronger. However, on the reduced surface, where binding was earlier predicted to be more physisorptionlike by using a standard generalized gradient approximation (GGA) approach, the van der Waals interaction increases the adsorption energy by a larger factor. Furthermore, three different local-density approximation and GGA functionals are compared, as corrected with the van der Waals scheme. It is found that the correction brings those three to reasonably similar descriptions of adsorption on both surfaces.

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I. INTRODUCTION

Organic functionalization of semiconductor surfaces has raised attention due to their potential applications in molecular electronics, nanoscale lithography, and biosensors.^{1,2} Therefore, the nature and detailed understanding of the adsorption becomes important, explaining such interface properties as molecular orientation,^{3,4} orbital energy alignment,^{4,5} and charge carrier injection through the interface.⁶⁻⁸

For the reasons above, we have recently studied adsorption of small hydrocarbon molecules⁹ and benzene¹⁰ on the tin dioxide SnO_2 (110) surface. Tin dioxide as a substrate is a multifunctional material and it shows many unique optical and electrical properties, making it good for chemical sensors, transparent conducting electrodes, and various nanodevices.¹¹⁻¹⁵

We have found the Kohn-Sham density functional theory^{16,17} (DFT) to be a robust method for calculations of the properties of such extended systems. However, allowing for proper nonlocality in the exchange and correlation functionals leads to better quantitative description of system properties and the energetics, in particular. The former we found essential in description of excitation energies of band-gap materials¹⁸ and the latter one in description of physisorption. We found the benzene adsorption onto the oxygen-poor surface of tin dioxide to be physisorptionlike with a flat adsorption potential along the surface,¹⁰ while the oxygen-rich surface showed weak covalent and ionic bonding features in attraction.

Therefore, in the present work we return to our previous study and include the van der Waals interaction (vdW) with the electronic correlations in terms of the nonlocal correlation kernel as presented by Dion *et al.*¹⁹ It has become a popular functional (vdW-DF) for calculations of adsorption²⁰⁻²⁵ and has been successfully used in several cases in which the standard functionals fail, such as benzene dimers, graphite, polymers, and especially organic molecules on surfaces. A comprehensive overview is given in Ref. 20.

The chosen vdW-DF¹⁹ has a special nonlocal kernel, constructed to include dispersion interactions at the *ab initio* level. Van der Waals attraction manifests dynamic intercorrelation

between electronic charges in two separate moieties at a nonoverlapping distance. Even so, due to the Hohenberg-Kohn theorem, it must be correctly described from the density only. The inverse problem of obtaining the external potential and the total energy from the density is challenging, as the changes to the density due to the vdW correlation are subtle. In fact, there is very little difference in total energies from perturbative and self-consistent vdW-DF energy evaluations²⁶—an observation, which we also confirm in this study.

Due to the distinct nonlocality, the vdW correlations are not accessible by the conventional DFT calculations with the local-density approximation (LDA) or generalized gradient approximation (GGA) type functionals. To assess the energetics and other effects from the vdW-DF we carry out a comparative study of performance of some exchange-correlation functionals with and without this kernel and analyze again the adsorption of benzene on the SnO_2 surface with the vdW-DF.

Our study is carried out using a new grid-based projector augmented wave code (GPAW).^{27,28} In the next section we describe the model surfaces, computational methods, and the computer code we use. In the third section we present the results and the analysis, and conclusions are given in the last section.

II. MODEL AND METHODS

The (110) termination of the tin dioxide surface has the lowest surface energy. Therefore, it is the most stable and suitable for applications but also for computational analysis.^{9,10,14,15,29-31} We have chosen the two ideal surfaces with the (110) termination for our study, the stoichiometric and the reduced ones. The stoichiometric surface forms under oxygen-rich conditions. However, formation of reduced surfaces is more complex which results in different surface reconstructions with varying amounts of oxygen and defects. Thus, what we consider in this study can be regarded as two model surfaces: the reduced one having high surface energy and being unlikely to form as such, and the stoichiometric one being the most stable under oxygen-rich conditions allowing

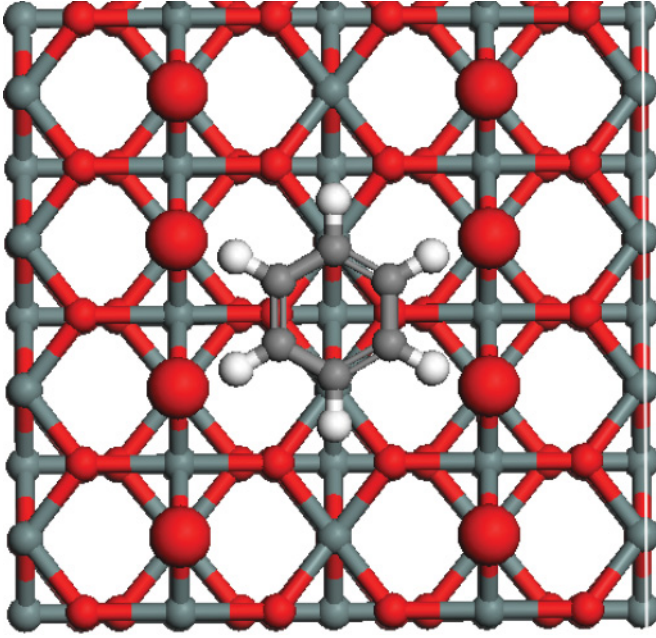


FIG. 1. (Color online) Adsorption site of benzene on top of the bridge site between two so called fivefold tin atoms in the surface layer. The “molecular diagonal” or two of the hydrogen atoms are aligned along the rows of bridging oxygen atoms. The difference between the two considered surfaces is the bridging oxygen atoms (large balls), absent from the reduced surface and present on the stoichiometric surface.

assessment of the effects and influence of the bridging oxygen atoms to the surface properties of SnO_2 . We expect these two limiting cases to give insight for understanding and interpretation of properties of other (110) surfaces with the intermediate oxygen abundance.

We use a slab model that is periodic along the surface and nonperiodic perpendicular to the surface. Our model is a 4×2 surface unit cell with periodic boundary conditions (see Fig. 1). This ensures that neighboring benzene molecules do not interact. We used 2×2 k -points in periodic directions within the Monkhorst-Pack scheme. The slab thickness is five layers of Sn atoms with 6 Å or more vacuum on both sides. Thus, the present model is essentially the same as the one in our previous study,¹⁰ except for the removed periodicity perpendicular to the surface. From our previous and more extensive study we have chosen one particular adsorption site of benzene, which is the most relevant for both surfaces. This bridge site between two “fivefold” surface tin atoms and the adsorption geometry is shown in Fig. 1. These tin atoms are fivefold bound to the oxygen atoms around. The other surface tin atoms are fourfold or sixfold in the reduced and stoichiometric surfaces, respectively.

With the Perdew-Burke-Ernzerhof GGA functional (PBE)³² we have previously found this adsorption site and orientation to be the most stable with the adsorption energy 0.62 eV at the stoichiometric surface, resulting from partly covalent and partly ionic bonding.¹⁰ At the reduced surface the adsorption energy has been found to be around 0.1 eV at this and the other sites and orientations. For more details see our previous study.¹⁰

The electronic structure calculations are carried out within the conventional DFT formalism, except for inclusion of the dispersion interaction in the form of the vdW-DF approximation.¹⁹ However, we would like to stress that the vdW-DF gives general nonlocal correlation not restricted just to vdW forces. Thus, the exchange-correlation energy is written as

$$E_{xc}^{\text{vdW-DF}} = E_x^{\text{GGA}} + E_c^{\text{LDA}} + E_c^{\text{nl}}, \quad (1)$$

where the exchange E_x^{GGA} is taken from a semilocal GGA functional. We use the GPAW implementation of the vdW-DF,²⁴ where revised PBE (revPBE) (Ref. 33) exchange functional is used. The local part of the correlation is taken from the LDA and the nonlocal correction to correlation is

$$E_c^{\text{nl}} = \frac{1}{2} \int d\mathbf{r}_1 \int d\mathbf{r}_2 n(\mathbf{r}_1) n(\mathbf{r}_2) \phi(q_1, q_2, r_{12}). \quad (2)$$

Here, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, and q_1 and q_2 are functions of density $n(\mathbf{r})$ and its gradient $\nabla n(\mathbf{r})$. For uniform densities the total correlation reduces to the LDA, since the nonlocal contribution E_c^{nl} vanishes.

For all calculations we use the GPAW code^{27,28} using grid spacing around $h = 0.2$ Å. GPAW allows use of periodic boundary conditions laterally and the “zero-boundary condition” at the vacuum boundary. Due to the large surface supercell two inequivalent Monkhorst-Pack k points were found to be sufficient sampling of the lateral first Brillouin zone.

First, the bulk unit cell geometries were relaxed without the vdW-DF, i.e., with the GGA functional, to find the bulk lattice constant for the slab model. Next, the slab geometries were similarly relaxed for both surfaces with the centermost slab layer fixed to the bulk geometry. To avoid finite grid-spacing and periodic image effects, the same numerical grid and periodicity were used to relax the benzene molecule. Some eggbox effects always remain in real space grid methods despite the advanced methods of GPAW,^{27,28,34} such as Fourier filtering of the localized functions. To control the eggbox effect, the relaxed benzene molecule was placed onto the surface with adsorption distance differences being exact multiples of the grid point spacing. This removes the eggbox error from the adsorption energy, which is a small difference of large total energies.

Though adsorption potential energy curves describe the long-range interaction energetics in detail, such curves are problematic to evaluate. Some part of the adsorbate-surface geometry has to be frozen to define and keep the adsorption distance in a static model. Thus, only partial geometry relaxation can be allowed, the full relaxation always leading to global or local energy minima and, thereby, to the adsorption height by definition.

We have chosen to evaluate the potential energy curves with single-point self-consistent field (SCF) calculations for the initially relaxed, but now frozen molecule and surface, with fixed C_6 ring-Sn_{sf} plane distances, first without vdW-DF. Then, the vdW potential energy curves were obtained with a post-SCF vdW correction, done in a perturbative way (-vdW lines in Fig. 2). Thus, these energies along the potential curves are neither fully relaxed with respect to the adsorbate-surface interaction nor SCF with respect to vdW-DF. To assess the post-SCF error for one of the geometries (revPBE) these

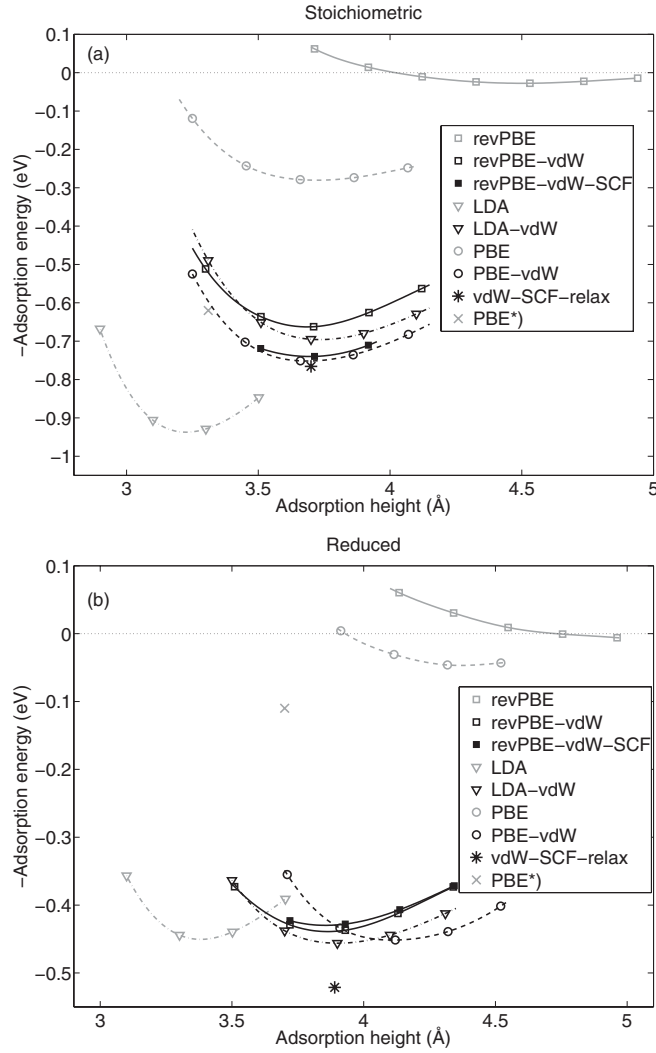


FIG. 2. Adsorption energy as a function of adsorption height on the (a) stoichiometric and (b) reduced surfaces. The data without (grey) and with (black) the vdW-DF are shown. The energies are evaluated from the single-point calculations, as described in text, and the vdW contributions, where indicated, are added post-SCF in a perturbative fashion. The stars (*), however, present data from fully relaxed geometries from SCF calculations with the revPBE + vdW-DF functional. The crosses (x) are the data from Ref. 10. The adsorption height is measured from the layer of the surfacemost fivefold tin atoms to the C_6 ring of benzene molecule.

calculations were carried out to self-consistency (revPBE+vdW-SCF in the figure). Calculation of fully relaxed minimum energy conformation with SCF vdW-DF is relatively time-consuming, but it gives the most essential qualitative and quantitative description of adsorption. These calculations were done for both surfaces (vdW-SCF-relax in the figure).

The revPBE functional has been successfully used in previous vdW studies (see Ref. 26 and references therein). To compare with those, we chose to adopt this functional for our study. However, to compare with our previous studies and, also, to make comparison of different functionals, we performed most of the calculations with the PBE (Ref. 32) and LDA functionals too.

TABLE I. Benzene adsorption energies and distances from the stoichiometric and reduced surfaces from calculations with the different functionals: LDA/GGA without (—) and with (vdW) the van der Waals functional. “SCF-relax” indicates full geometry relaxation within the SCF calculation, like in Fig. 2.

Stoichiometric	Height (Å)		Energy (eV)	
	—	vdW	—	vdW
LDA	3.19	3.67	0.93	0.70
PBE	3.62	3.66	0.28	0.75
revPBE	4.50	3.68	0.03	0.66
revPBE SCF		3.70		0.74
vdW-DF SCF-relax		3.70		0.77
PBE SCF-relax ¹⁰	3.3		0.62	
Reduced	—	vdW	—	vdW
LDA	3.40	3.85	0.45	0.46
PBE	4.36	4.05	0.05	0.45
revPBE	—	3.85	—	0.44
revPBE SCF		3.85		0.43
vdW-DF SCF-relax		3.89		0.52
PBE SCF-relax ¹⁰	3.7		0.11	

III. RESULTS

The two bulk lattice constants a/c were found to be 4.78/3.21, 4.89/3.26, and 4.94/3.27 Å from energy minimization with the functionals LDA, PBE, and revPBE, respectively. Earlier with PBE, atomic basis set, and another software we found 4.82/3.29 Å.¹⁰

The bulk data compare well with the experimental lattice constants $a = 4.74$ and $c = 3.19$ Å and also reflect the usual performance and accuracy of the semilocal functionals. Optimization of the periodic slab with the 4×2 surface supercell and the centermost slab layer fixed to the above bulk geometry gives essentially the same pristine surface relaxation as earlier.¹⁰

All evaluated adsorption potential curves are shown in Figs. 2(a) and 2(b). The remaining eggbox effect due to the numerical grid was found to cause oscillation within some hundredths of eV. This is eliminated as described previously. The minimum energy of each potential curve was found by fitting a parabola to the three to five lowest energies. The fitted adsorption data are given in Table I.

First, we note that our approach to evaluating the adsorption curves with frozen conformations, but varying adsorption distance as described previously, is successful, as expected. The molecule and the surface are stiff enough for such an approximation, and the adsorption data in Table I are changed only a little in full relaxation. The adsorption height remains essentially the same and the adsorption energy is increased 0.03 eV for the stoichiometric surface and 0.09 eV for the reduced surface.

We see that for both surfaces the three post SCF vdW-DF corrected adsorption data look similar independent of the initial functional. The three potential curves become grouped together despite the major differences in the adsorption without the vdW-DF. This is also expected, because the only differences left are in the nonrelaxed geometries and electron densities, both being very small. Thus, the average adsorption

energies are 0.75 and 0.52 eV, and the distances are 3.7 and about 4.0 Å for the stoichiometric and reduced surfaces, respectively.

On the contrary, the data without the vdW-DF behaves as usual: the LDA binds much stronger than the GGA, and, furthermore, differently at the two surfaces. At the stoichiometric surface, where the binding is partly covalent and partly ionic¹⁰ the LDA overbinds strongly with large adsorption energy and short distance, and the addition of vdW-DF leads to weakening of the binding. Also, at the reduced surface the LDA binds too close but fortuitously the energy appears to become the same as the one predicted by including the vdW-DF correction. We note that Vanin *et al.*²³ found similar behavior in the case of graphene adsorption onto metal surfaces: on weakly bonded systems, the binding energies obtained with the LDA were found to be similar to those from vdW-DF corrected calculations, but significantly larger in the case of strongly bonded systems. Also, the binding distance behaves similarly: too short with the LDA. Thus, it is worth of emphasizing that binding described by the LDA is incorrect and different from that of the other functionals as also seen from the curvature of the adsorption potential.

The fully relaxed SCF vdW-DF calculations give adsorption energies of 0.77 and 0.46 eV and distances of 3.70 and 4.3 Å for the stoichiometric and reduced surfaces, respectively. These data match good enough with that from the separately relaxed post-SCF vdW-DF data, see above, to allow us to conclude about the good reliability of these much simpler and less heavy single-point calculations for potential curves. Thus, neither partial relaxation with the fixed distance approaches nor SCF vdW-DF approaches are necessarily needed for insight or evaluation of the potential curves and related dynamics. Also, it should be kept in mind that with static models the evaluation of such curves always requires artificial freezing of one or more degrees of freedom.

In our previous study¹⁰ with the PBE functional, the adsorption of benzene on the stoichiometric surface is clearly chemisorption in nature and displays both ionic and covalent character. However, on the reduced surface, the binding is negligible (~ 0.1 eV) and is interpreted to be dominated by physisorption. The related adsorption data from the previous PBE calculation are also shown in Fig. 2 (crosses) and listed in Table I.

By using the vdW-DF on the stoichiometric surface we find that this picture remains basically unchanged, but the quantitative data can be refined. Both the adsorption energy and the distance become nonnegligibly larger, to 0.77 eV and 3.7 Å, respectively. On the reduced surface, where

the physisorption is relatively more important, the vdW-DF brings relatively more changes. The adsorption height increases only slightly to 4.3 Å but the adsorption energy increases to 0.52 eV. However, the absolute changes at the different surfaces are not that dramatic, which probably reflects the seamlessness¹⁹ of the vdW-DF in describing the balanced transition from dominance from local to nonlocal electronic correlation phenomena.

IV. CONCLUSIONS

Our study demonstrates the usefulness of the DFT functional including the nonlocal vdW interaction by Dion *et al.*¹⁹ in the considered case, benzene molecule adsorption on the rutile phase tin dioxide (110) surface. The oxygen-rich stoichiometric and oxygen-poor reduced surfaces present chemisorption and physisorption as challenging test cases for this vdW-DF to differentiate between the two. In this respect we find a good performance of the chosen vdW-DF, describing a seamless transition from one to the other.

Compared to our previous study with the conventional GGA type PBE functional we find that on the stoichiometric surface, where binding clearly has both a covalent nature and an ionic nature, the physical picture is not changed by adding the vdW interaction, as expected. However, on the reduced surface, where the binding is more physisorptionlike, the vdW interaction adds relatively more to the adsorption energy and distance.

In comparison of the different functionals of type LDA or GGA we find that without vdW-DF the adsorption curves vary considerably. However, with the vdW-DF correction the curves become similar enough to give essentially the same adsorption energies and geometry. Obviously, this is because of the remaining small differences in the geometry and densities.

Finally, in the case of benzene, we find heavy calculations with full geometry relaxation and a SCF account of vdW-DF less important, but we find post-SCF vdW-DF evaluation sufficient for calculations of the adsorption potential curves with partial relaxation, i.e., freezing the distance stepwise. Obviously, this conclusion does not apply to larger or more flexible adsorbates, in general.

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