

# Benzene Adsorbed on Metals: Concerted Effect of Covalency and van der Waals Bonding

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The adsorption of aromatic molecules on metal surfaces plays a key role in surface science and functional materials. Depending on the strength of the interaction between the molecule and the surface, the binding is typically classified as either physisorption or chemisorption. Van der Waals (vdW) interactions contribute significantly to the binding in physisorbed systems, but the role of vdW energy in chemisorbed systems remains unclear. Here, we demonstrate that the binding of strongly adsorbed benzene molecule to metal surfaces arises from a concerted effect of covalent interactions and vdW bonding. Notably, vdW forces contribute more to the binding of covalently bonded benzene molecule than they do when benzene is physisorbed.

The adsorption of aromatic molecules at transition-metal surfaces is important for fundamental and applied surface science studies [1–3], and these systems show promise as components in (opto)-electronic devices [4]. In the case of weak overlap of electron orbitals between the adsorbate and the substrate surface, the ubiquitous van der Waals (vdW) interactions is frequently the only force that binds the molecule to the surface. This situation is typically referred to as physisorption. In the chemisorption case, the covalent or ionic bonding dominates and the effect of vdW interactions on the overall strength of adsorption is typically assumed to be weak. In this Letter, we challenge this conventional view, by demonstrating the significantly larger contribution of vdW energy to the stabilization of strongly adsorbed benzene on (111) surfaces of Pt, Pd, Rh, and Ir metals when compared to physisorption on Ag(111) and Au(111) surfaces.

Until the recent developments (see, *e.g.*, Refs. [5–8]) for efficiently incorporating the long-range vdW energy within density-functional theory (DFT) calculations it was not possible to determine the role of the vdW energy for extended systems and adsorption processes [9–11]. A large majority of previous theoretical work on vdW interactions mainly focused on weakly bound systems [12–18]. Typical examples include benzene (Bz) adsorbed on the Ag(111) and Au(111) surfaces [15–18], and noble gases on the Cu(111), Ag(111), Pt(111), and Pd(111) surfaces [10, 19–21]. A unifying aspect of these studies is the observation that the inclusion of vdW interactions into standard DFT within the generalized gradient approximation (GGA) often brings a large increase in binding, and results in a much better agreement with experimental adsorption distances and energies. However, the vdW forces can also have a *qualitative* impact on the adsorption process. One particularly interesting example was reported by Blügel’s group, showing that the

vdW forces are the key ingredient to trigger the binding of pyridine on Cu(110) from physisorption to weak chemisorption [22]. Mittendorfer *et al.* [23] reported a novel mechanism for graphene adsorption on Ni(111), where weak covalent and vdW interactions lead to two different minima in the binding curve. Another example was shown in our recent work on the isophorone molecule (C<sub>9</sub>H<sub>14</sub>O) at the Pd(111) surface, which illustrated that the binding structure and the dehydrogenation pathway in this system can be predicted only after accounting for the vdW interactions [24]. In this Letter, we study the nature of adsorption for molecules forming strong covalent bonds with metal surfaces, *i.e.* systems where even a standard GGA functional is expected to work. Our calculations demonstrate the significant concerted effect of covalent bonding and vdW interactions for such systems, predicting a greater contribution of vdW interactions to the stability of strongly adsorbed systems when compared to weakly physisorbed systems. We also provide compelling evidence that recently developed methods for including vdW interactions in DFT [8, 10] allow quantitative treatment of both weakly and strongly adsorbed aromatic molecules on metal surfaces.

The typical strongly bound Bz/Pt(111) system (adsorption energy 1.57-1.91 eV [25]) and the typical weakly bound Bz/Au(111) system (adsorption energy 0.73-0.87 eV [26]) are used first to demonstrate our point. Accurate experimental data is available for both of these systems, enabling direct quantitative verification of our theoretical calculations. We used two different vdW-inclusive approaches in the present work: a newly developed PBE+vdW<sup>surf</sup> method [10], as implemented in the FHI-aims all-electron code [27]; and the optB88-vdW method [8], as implemented in the VASP code [28, 29]. The PBE+vdW<sup>surf</sup> approach includes screened vdW interactions (beyond the pairwise atom-atom approximation) to study adsorbates on surfaces, by a synergetic

linkage of the PBE+vdW method [6] for intermolecular vdW interactions with the Lifshitz-Zaremba-Kohn theory [30] for the dielectric screening within the metal substrate. The optB88-vdW method is a modified version of the vdW-DF functional [5], by using the optB88 exchange functional instead of the too repulsive revPBE functional. Both PBE+vdW<sup>surf</sup> and optB88-vdW methods can accurately describe intermolecular interactions with mean absolute relative errors on the order of 9% [8, 31] compared to coupled-cluster dimer binding energies for the S22 molecular database. Remarkable performance has also been reported for solids and weakly adsorbed molecules on surfaces when using PBE+vdW<sup>surf</sup> and optB88-vdW methods [10, 11, 29, 32]. For comparison purposes, calculations using the vdW-DF functional and its second version (vdW-DF2) [33] were also carried out for the Bz/Pt(111) and Bz/Au(111) systems.

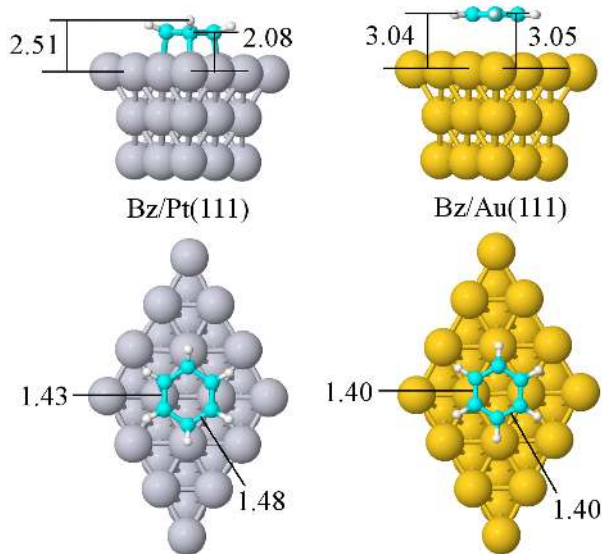


FIG. 1. Adsorption structures of the Bz/Pt(111) system and Bz/Au(111) system, both at the so-called  $\text{bri}30^\circ$  adsorption site (see text). We carried out extended periodic calculations, but only a small part of the supercell is shown. Six metal layers were used but only the topmost three layers are depicted in the figure. The indicated distances (Å) are obtained based on the PBE+vdW<sup>surf</sup> optimized structures. Gray, yellow, cyan, and white spheres represent Pt, Au, C, and H atoms, respectively. Optimized lattice constants were used for every method.

To demonstrate the differences in the adsorption mechanism, we explore the potential-energy surface (PES) for Bz on the Pt(111) and Au(111) surfaces. We place a single Bz molecule at the eight high-symmetry adsorption sites of the (111) metal surface [39], followed by geometry relaxation. The metal surfaces are represented by 6-layer slabs with a  $(3 \times 3)$  unit cell, with no reconstruction of Pt(111) and Au(111) (further calculation details are included in the supplemental material). The

TABLE I. Comparison of adsorption energy ( $E_{\text{ad}}$ ) and average perpendicular heights ( $d_{\text{CM}}$  and  $d_{\text{HM}}$  for carbon-metal and hydrogen-metal, respectively) between DFT calculations and experimental data for Bz on Pt(111) and Au(111). The distances are referenced to the average positions of the relaxed topmost metal atoms. The adsorption energy  $E_{\text{ad}}$  is defined as  $E_{\text{ad}} = -(E_{\text{AdSys}} - E_{\text{Me}} - E_{\text{Bz}})$ , where the subscripts *AdSys*, *Me*, and *Bz* denote the adsorption system, the clean metal substrate, and the isolated Bz molecule, respectively.

System	Method	$E_{\text{ad}}$ [eV]	$d_{\text{CM}}$ [Å]	$d_{\text{HM}}$ [Å]
Bz/Pt(111)	PBE+vdW <sup>surf</sup>	1.96	2.08	2.51
	optB88-vdW	1.84	2.12	2.53
	vdW-DF	0.77	2.16	2.57
	vdW-DF2	0.34	2.20	2.65
	PBE	0.81	2.10	2.54
	LDA	2.30	2.05	2.47
	Experiment	1.57-1.91 <sup>a</sup>	2.02±0.02 <sup>b</sup>	-
Bz/Au(111)	PBE+vdW <sup>surf</sup>	0.74	3.05	3.04
	optB88-vdW	0.79	3.23	3.23
	vdW-DF	0.59	3.44	3.42
	vdW-DF2	0.56	3.29	3.27
	PBE	0.15	3.62	3.62
	LDA	0.49	2.83	2.82
	Experiment	0.73-0.87 <sup>c</sup>	2.95-3.10 <sup>d</sup>	-

<sup>a</sup> Heat of adsorption measured with calorimetry, at the same coverage (0.7 ML) used for the DFT calculations [25]. The error estimates of  $\pm 10\%$  are taken from Ref. [25]. Recent work suggests reduced errors of  $\pm 5\%$  [34].

<sup>b</sup> LEED experiment [35].

<sup>c</sup> TPD experiment [10, 26].

<sup>d</sup> Deduced data based on the experimental workfunction for Bz on Au(111) and adsorption distance for pentacene on Au(111) [18, 36, 37].

adsorption geometries and energies for Bz on Au(111) and Pt(111) at the preferable adsorption site are shown in Fig. 1 and Table I. Already here one can clearly distinguish the different nature of bonding for the adsorption of Bz on Pt(111) and Au(111). Irrespective of the functional used (PBE, PBE+vdW, and PBE+vdW<sup>surf</sup>), the  $\text{bri}30^\circ$  is the most preferable site for Bz/Pt(111), with an angle of  $30^\circ$  between the C-C and Pt-Pt bonds, see Fig. 1. This result is consistent with previous periodic slab GGA calculations [39–42], as well as low-energy electron diffraction (LEED) [35] and scanning tunneling microscopy (STM) [43] experiments. Moreover, the PES shows a corrugation of 1.33 eV for Bz/Pt(111) when using PBE+vdW<sup>surf</sup>. In contrast, the PES for Bz/Au(111) is found to be flat, with only 0.04 eV corrugation. This result further justifies the STM observations that even at a temperature of 4 K, Bz molecules are capable of diffusing over the Au(111) terraces [44].

The analysis of the equilibrium distances and adsorption energies in Table I demonstrates that both PBE+vdW<sup>surf</sup> and optB88-vdW methods lead to an excellent agreement with the available experimental data. For the Bz/Pt(111) system, the PBE+vdW<sup>surf</sup> adsorption energy of 1.96 eV is close to that from optB88-

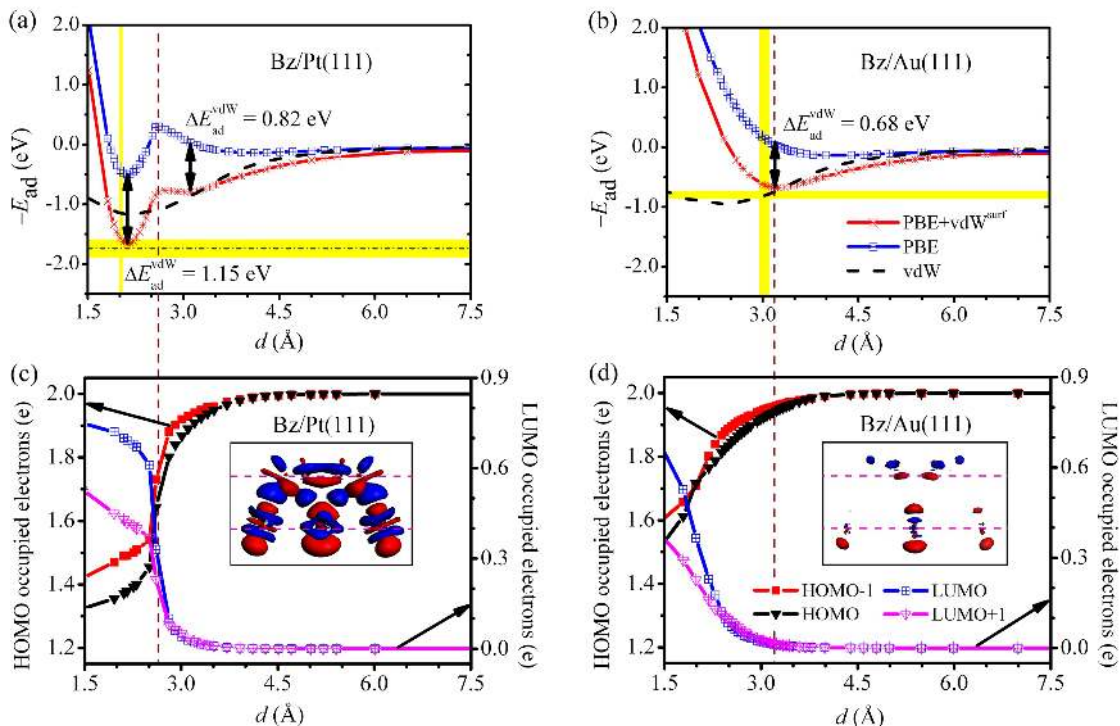


FIG. 2. Top: Adsorption energy  $-E_{\text{ad}}$  as a function of the adsorption height  $d$  for Bz on Pt(111) (a) and on Au(111) (b) from the PBE and PBE+vdW<sup>surf</sup> methods (the carbon backbone height  $d$  from the surface is kept fixed). The experimental binding distances and adsorption energies are indicated by yellow intervals. Bottom: Integrated projected molecular density of states [38] for the HOMO-1, HOMO, LUMO, and LUMO+1 orbitals of the benzene molecule as a function of  $d$  for Bz on Pt(111) (c) and on Au(111) (d). The inset in panel (c) shows a side view of the electron density difference, which was obtained by subtracting electron density of isolated molecule and clean surface from an electron density plot of the entire adsorbed system, upon Bz adsorption on Pt(111) at  $d=2.08$  Å (red = electron depletion, blue = electron accumulation). For the same value of the isosurface ( $0.04 \text{ \AA}^{-3}$ ), the electron density difference for Bz/Au(111) at  $d=2.08$  Å is significantly weaker, see the inset in panel (d).

vdW (1.84 eV) and both methods agree with the measured calorimetry values at 0.7 ML (1.57-1.91 eV, the same coverage used for DFT calculations) [25]. The PBE+vdW<sup>surf</sup> adsorption energy converges to 2.18 eV with increasing surface cell size, within the error bar of calorimetry measurements in the limit of zero coverage (1.84-2.25 eV) [25]. Note that the exclusion of the vdW interactions in the *strongly adsorbed* Bz/Pt(111) system would lead to a significant reduction in the binding energy (0.81 eV from PBE), in disagreement with the experimental data. Remarkably, the adsorption energies computed using the vdW-DF and vdW-DF2 methods are even smaller than calculated with PBE. The adsorption energy for Bz adsorbed on the Au(111) surface is considerably smaller than that of Bz/Pt(111). Also for Bz/Au(111), the PBE+vdW<sup>surf</sup> adsorption energy (0.74 eV) agrees very well with both the optB88-vdW result (0.79 eV) and the experimental temperature-programmed desorption (TPD) data at 0.1 ML (0.73-0.87 eV) [10, 26]. We conclude that PBE+vdW<sup>surf</sup> and optB88-vdW methods yield quantitative agreement with experimental adsorption distances and energies for both

weakly and strongly adsorbed Bz molecule. In contrast, local-density approximation (LDA) calculations are not systematic, underbinding for Au(111) and overbinding for Pt(111).

Deeper insight into the mechanism of Bz adsorption can be gained upon analysis of the binding energy curves,  $E_{\text{ad}}(d)$ , in Fig. 2. The binding energy curves exhibit several characteristic effects. With decreasing distance the binding energy of the adsorbate system increases, determined mainly by vdW interactions, and here (for  $d > 3.5$  Å) Au(111) and Pt(111) show very similar behavior. In both cases the calculations show a small broadening of the energy levels. The fully occupied  $d$ -band of Au is obviously stiffer than the partially empty  $d$ -band of Pt. In fact, for the latter the Pauli repulsion can be weakened by the rearrangement of  $d$ -electron density (a similar effect has been investigated in Ref. [19]). As a consequence, the Bz molecule gets closer to the surface of Pt and the HOMO and LUMO levels of the combined system broaden and hybridize noticeably. This goes together with significant electron transfer: The HOMO and HOMO-1 orbitals of Bz molecule get partially depleted

and the LUMO and LUMO+1 orbitals become partially filled. This behavior (broadening, shift, hybridization of levels, and electron transfer) is a clear signature of the covalent interaction for Bz/Pt(111). Thus, at the adsorption geometry the wave-function has attained a qualitatively new character. Figure 2 shows that this character change sets in for Pt at a distance of 3.1 Å. At 2.6 Å nearly a full electron has been transferred from the HOMO and HOMO-1 levels to the LUMO and LUMO+1 levels, and in the total energy we observe a “phase transition behavior” (cf. the peak at 2.6 Å). Finally, at the equilibrium geometry the electron transfer (rearrangement) is as large as  $\sim 1.1$  electrons. For Au surface the process is much weaker and – not surprisingly – a covalent contribution to the adsorption process remains negligible. Thus, the vdW attraction governs the interaction.

Further inspection of the electron density difference at the strongly bound minimum for Bz/Pt(111) in Fig. 2(c) demonstrates the rather strong hybridization between the HOMO/LUMO orbitals of Bz and the  $d_{z^2}$  orbitals of the Pt(111) atoms. For the same adsorption height, the electron density difference for Bz/Au(111) is weak (see Fig. 2(d), inset). The presence of two minima for Bz/Pt(111) resembles the recently studied bonding of graphene on Ni(111) [23, 45]. However, the adsorption of Bz on Pt(111) exhibits a different feature. In fact, Bz is exothermically bound on Pt(111) already when using PBE without vdW interactions, while the PBE adsorption energy is endothermic for graphene on Ni(111).

Interestingly, while covalency is crucial for the Bz/Pt(111) bonding character, energetically the vdW contribution is in fact significant. It lowers the adsorption energy from 0.50 eV (pure PBE result) to 1.65 eV (PBE+vdW<sup>surf</sup>) in Fig. 2. Thus the final adsorption results from a strongly concerted, synergistic effort. Upon comparing the binding curves for Bz/Pt(111) and Bz/Au(111) we see that the vdW contribution (due to vdW<sup>surf</sup>) for Bz/Pt(111), 1.15 eV, is even stronger than that for Bz/Au(111), 0.68 eV. The Bz/surface vdW interaction  $C_3$  coefficient is essentially the same for Pt(111) and Au(111) surfaces (2.17 and 2.02 hartree bohr<sup>3</sup>, respectively). Therefore, we conclude that the larger contribution of the vdW energy in the case of covalent bonding comes from the rather short adsorption distance of the Bz molecule from the surface.

Our conclusions hold in general for the adsorption of Bz on other transition metal surfaces. For Bz adsorbed on the Pd(111), Rh(111), and Ir(111) surfaces, the vdW energy contributions from the PBE+vdW<sup>surf</sup> method are in the range of 0.97-1.21 eV, greater than those for Bz physisorbed on Ag(111) and Au(111) (0.68-0.82 eV). Even larger vdW energies are found in more complex polyaromatic adsorption systems. For instance, the vdW energy is determined to be 1.77 eV for naphthalene (C<sub>10</sub>H<sub>8</sub>) on the Pt(111) surface with (5 × 4) unit cell. Also for this case the calculated adsorption energy from

TABLE II. Adsorption energies  $E_{\text{ad}}$  (eV) of Bz adsorbed on (111) surfaces of Ag, Pd, Rh, and Ir.

System	PBE	PBE+vdW <sup>surf</sup>	optB88-vdW
Bz/Ag(111)	0.09	0.75	0.72
Bz/Pd(111)	1.17	2.14	1.91
Bz/Rh(111)	1.48	2.52	2.27
Bz/Ir(111)	1.10	2.24	2.09

PBE+vdW<sup>surf</sup> (2.91 eV) is within the experimental error bars (2.80-3.42 eV) [46]. For anthracene (C<sub>14</sub>H<sub>10</sub>) on the Pt(111) surface with (6 × 4) unit cell, the adsorption energy contributed by vdW interactions (2.42 eV) largely exceeds that determined from the PBE functional (1.38 eV).

In summary, we have demonstrated the concerted effect of covalency and vdW bonding for benzene strongly adsorbed on metal surfaces using two different vdW-inclusive DFT methods. The vdW energy in Bz/Pt(111), a typical strongly adsorbed system, is almost 0.5 eV greater than that in Bz/Au(111), a typical physisorbed system. Our findings indicate that DFT calculations with dispersion interactions are essential even in the case of rather strong covalently bound molecules on surfaces.

We are grateful for support from the FP7 Marie Curie Actions of the European Commission, via the Initial Training Network SMALL (MCITN-238804). W.L. was funded by a fellowship from the Alexander von Humboldt Foundation. A.T. acknowledges support from the European Research Council (ERC Starting Grant VDW-CMAT). A.M. is supported by the ERC (ERC Starting Grant QUANTUMCRASS) and by the Royal Society through a Wolfson Research Merit Award. J.C. is a Ramón y Cajal fellow supported by the Spanish Government.

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