Trends in adsorption characteristics of benzene on transition metal surfaces: Role of surface chemistry and van der Waals interactions

Yildirim, Handan ; Greber, Thomas ; Kara, Abdelkader

Abstract: The accurate description of interface characteristics between organic molecules and metal surfaces has long been debated in theoretical studies. A well-founded description of interface geometry and adsorption energy is highly desirable for these hybrid inorganic/organic interfaces. Using first principles calculations with the inclusion of five van der Waals functionals (vdW-DF family), benzene (C_6H_6) adsorption on seven transition metal surfaces is studied to explore the performance of these vdW functionals under varying surface chemistry. Our results reveal that vdW interactions are crucial for an accurate description of bonding on transition metal substrates. We find that vdW interactions increase adsorption energy on coinage metal surfaces (Au, Ag, Cu) by about 0.7 eV, while they lead to even larger increases in the adsorption energies on the reactive transition metal surfaces (Pd, Pt, Rh, Ni). Our calculations also reveal that changes in adsorption energies stemming from vdW functionals show significant variation, and can be grouped. We find the adsorption energies and heights on the reactive transition metal surfaces obtained using vdW-DF and vdW-DF2 functionals to differ significantly from those of the opt-type functionals, revealing the intrinsic strong repulsion character at short ranges for the former functionals. A simple comparison between experimentally determined adsorption energies (averaged) and those of computed suggests that optPBE and optB88 functionals show systematically good agreement. The information acquired from our analysis on the performance of these functionals can be used as a basis for further refinement of these functionals for the adsorption on metal surfaces with varying chemistry.

Trends in Adsorption Characteristics of Benzene on Coinage and Transition Metal Surfaces: *Role of Surface Chemistry and van der Waals Interactions*

Handan Yildirim[1*+], Thomas Greber[2], and Abdelkader Kara[1+]
1Physics Department, University of Central Florida, Orlando, FL
2Physik-Institut, Universität Zürich, Switzerland

Abstract

The accurate description of interface characteristics between organic molecules and metal surfaces has long been debated in theoretical studies. All proposed methods revealed the importance of van der Waals interactions. Using first principles calculations with the inclusion of five van der Waals functionals, Benzene (C_6H_6) adsorption on coinage and transition metal surfaces are studied to explore the performance of these functionals under varying surface chemistries. Our results reveal that van der Waals interactions are crucial for an accurate description of bonding not only for coinage, but also for transition metal substrates. Moreover, adsorption energy results stemming from these five functionals show significant variation, with a trend that allows a *grouping* based on the calculated adsorption strengths. A simple comparison between the averaged experimentally determined adsorption energies and those computed suggests that optPBE and optB88 functionals show systematically good agreements. The information acquired from our comprehensive analysis on the performance of these functionals is of broad interest, and in particular, can be used as a basis for further refinement of these functionals for varying surface chemistry.

I. Introduction

The nature of organic molecule interaction with metal surfaces is of broad interest for both fundamental and applied research. For environmental and industrial needs, petroleum refining and reforming processes, transformation of organic molecules into less hazardous components is crucial [1-2]; hydrogenation and cracking of these molecules can be performed by transition metal catalyst [3]. More recently, organic molecule interaction with metals has attracted attention as they show potential application in the design of devices based on electro-active organic molecules [4, 5]. Therefore, thorough understanding of this interaction is crucial, and is the starting point for any quantitative insight into a catalytic process.

Benzene is the smallest aromatic molecule, and has often been used as a model system. Although basic interaction characteristics with metals are fairly well understood, such important details as the adsorption site preferences, the accurate adsorption energies, and geometries are often non trivial to obtain from experimental studies. In particular, the interpretation of the experimental results on adsorption characteristics for transition metals is challenging due to possible fragmentation [6-10]. The experimental studies mostly reported changes in geometric and electronic structures, work functions, and vibrational properties upon adsorption. The available data on adsorption energies, however, is scarce; making the theoretical insights valuable, for a review see Ref. [11]. From the available literature on benzene adsorption on coinage metals [12-17], a common understanding is that benzene weakly interacts with these surfaces. For close-packed (111) coinage metal surfaces, the adsorption is dominated by van der Waals (vdW) forces, and defined as weak physisorption. On the other hand, the nature of adsorption on transition metals is significantly different, governed by both ionic and covalent bonding [1,2,18-24]. These conclusions obtained from the studies employing standard density functional theory (DFT), which is unable to describe long-range electron correlations (electron dispersion forces). The recent vdW implementations made it possible to incorporate these non-local correlations into the description of the nature of bonding [25-31]. The results revealed that inclusion of vdW interactions *in general* provides a better agreement with the experimental data. Although several studies have been conducted for assessing the importance of vdW interactions on adsorption, *most*

often, the conclusions are driven based on a small number of data set, involving limited number of surfaces, and explored only few vdW functionals. Thus, a systematic study exploring the adsorption on both coinage and transition metal substrates is necessary to gain a comprehensive understanding of the adsorption, while assessing the transferability of the vdW functionals for varying substrate chemistry. A similar attempt has been made by a recent study focusing on the role of vdW interactions for benzene adsorption on coinage and transition metal substrates [32]; however, the focus was not to assess exhaustively the performance of the available functionals, rather to provide comparative view on assessing their own methodology.

The main focus of the present paper is to give insights into how the interaction of benzene varies when the substrate characteristics are changed, and how the considered vdW functionals in this study treat the adsorption characteristics for chemically non-identical substrates. To our best knowledge, such a detailed study is lacking. Here, the adsorption characteristics of benzene on close packed (111) coinage (Ag, Cu, and Au) and transition metal (Pd, Pt and Rh, and Ni) surfaces are explored using both GGA functional of Perdew, Burke, and Ernzerhof (PBE) [33, 34], and those vdW functionals [35] available in the Vienna Ab-initio Simulation Package (VASP) [36-38]. Note that these functionals introduce the non-local correlations self-consistently, which is needed for accurate inclusion of these effects [39]. The calculations reveal that for physisorbed systems, the inclusion of vdW interactions enhance the adsorption energies regardless of the functionals used. For chemisorbed systems, on the other hand, much significant contribution to the adsorption energies is obtained for the three functionals (opt-types [28], less "repulsive" functionals within the vdW-DF scheme), however, this contribution is less significant for the two implementations (revPBE and rPW86, "strongly repulsive at short ranges" known as vdW-DF [25] and vdW-DF2 [40], respectively). For these functionals, the adsorption energies on transition metal substrates are reduced in comparison with those obtained using GGA-PBE. This can be understood from the strong repulsive nature at short range (see the discussion in Ref. [41]). The results reveal the role of vdW interactions on the accurate description of adsorption characteristics on metal substrates, even for strongly bound systems, however, the choice of which functionals to use is still debatable as there is wide range of energies obtained when using different

3

functionals. Overall, our results reveal the differences and similarities obtained for the adsorption energies and heights, between different functionals, and suggest the expected *grouping* of these functionals in two sets based on the trends obtained for the energies and the adsorption geometries.

II. Computational Details

The calculations are carried out within the DFT framework using the VASP code (version 5.2.12). For assessing the role of vdW interactions, and screen the transferability of the functionals, the calculations are performed using optB88 [28], optB86b [35], and optPBE [28], revPBE [25], and rPW86 [40] functionals, and the comparisons are made with the GGA-PBE results. The interaction between the valence electrons and ionic cores is described by the projector augmented wave (PAW) method [42,43]. The energy cutoff is set to 400 eV for the wave functions, and the Brillouin zone sampled with a 7x7x1 Monkhorst-Pack grid [44]. The calculated lattice constants are summarized in Table 1, and show excellent agreement with the previous theoretical results [35] and those of the experimental results with zero-point energy correction (ZPEC) [45]. A spin polarized calculations are performed for the adsorption on Ni(111).

Table 1. Calculated lattice constants (in Å) using vdW functionals and PBE. The experimental lattice constants with ZPEC are taken from Ref. 46.

Method	Ag	Au	Cu	Pt	Pd	Rh	Ni
PBE	4.154	4.170	3.635	3.980	3.960	3.842	3.525
optB86b	4.110	4.140	3.598	3.960	3.919	3.820	3.489
optB88	4.147	4.178	3.626	3.988	3.951	3.846	3.511
optPBE	4.179	4.197	3.648	3.999	3.970	3.858	3.529
revPBE	4.258	4.261	3.702	4.040	4.023	3.896	3.571
rPW86	4.329	4.352	3.747	4.117	4.091	3.957	3.610
Experiment	4.063[45]	4.061[45]	3.595[45]	3.913[45]	3.876[45]	3.793[45]	3.509[45]

We construct a (4×4) super cell structure of four layers with 19Å vacuum separating the two surfaces. The convergence of the adsorption energies is tested with additional calculations using a six-layers slab for a few systems. Our results suggest four layers slab to be sufficient for reaching similar conclusions. Upon adsorption of benzene, the bottom two layers are fixed during the optimization with a force criterion of 0.01 eV/Å. The most stable adsorption site is frequently reported to be the bri30^o both from

theoretical and experimental studies [1, 2, 19, 46-48]. Details are given in the Supplementary Information. For all calculations, benzene is brought at a relatively high distance (~3.5Å) from the surface, and regardless of the surface and the functional, the equilibrium geometry of benzene is the bri30^o site. All results reported here are obtained for the bri30^o adsorption configuration.
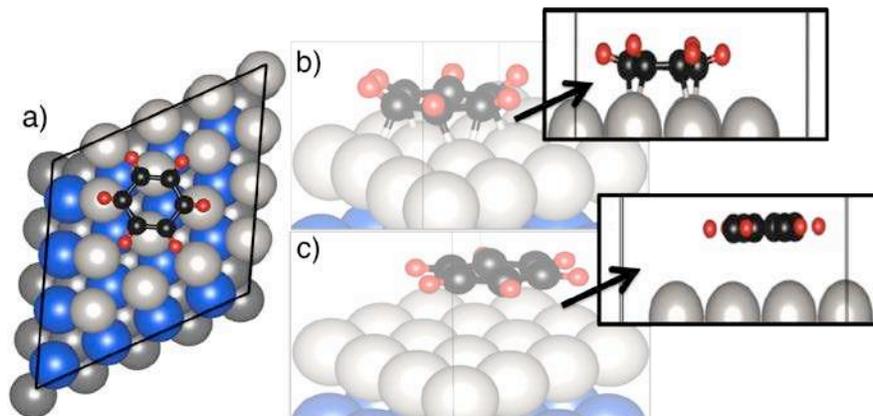

Figure 1. a) Top view of the bri30$^°$ configuration of benzene on (111), **b)** The equilibrium adsorption geometry on Pt(111), and **c)** The equilibrium adsorption geometry on Au(111). Light gray, blue, dark gray, red, and black spheres represent the first, the second, the third layer atoms, H, and C atoms, respectively.

III. Results and Discussions

Let us start with benzene adsorption heights on each substrate, which are summarized in Table 2. The adsorption heights on coinage metals are in *general* higher than those on the transition metal surfaces. In particular, the adsorption heights calculated using the opt-type functional is substantially smaller than those obtained using the revPBE, rPW86 functionals, and the PBE. This effect results from strong repulsive nature of revPBE and rPW86 functionals leading benzene to be adsorbed at higher distances from the surfaces. These functionals are known to cause too large intermolecular binding distances, and most often leading to inaccurate binding energies as discussed in a recent review article [41]. For the adsorption on transition metals, on the other hand, small reduction in the adsorption heights (from those of PBE) is found for all the surfaces when using the opt-type functionals, while an increase in binding heights is obtained for the revPBE and rPW86 functionals.

The adsorption energies on coinage and transition metal surfaces are plotted in

Figures 2.a-b with respect to vdW functionals, respectively. For coinage substrates, the Fig.2.a indicates that the adsorption energies systematically increase with the inclusion of non-local correlations, and among the functionals, the results obtained using opt-type functionals is higher than those calculated using revPBE and rPW86 functionals (see Fig.2.a and the Table 3). This trend correlates with that obtained for the adsorption heights (see Table 2). As the tables show, with the inclusion of vdW interactions, a significant reduction in adsorption heights (opt-type functionals) is accompanied by an increase in adsorption energies, while the change in the adsorption heights (from those of PBE) calculated using revPBE and rPW86 functionals is smaller.

Table 2. Benzene adsorption heights (in Å) - C-metal (d_{C-M}) and H-metal (d_{H-M}) distances. The distances are calculated from the average positions of the surface atoms.

Method	Bz/Ag(111)		Bz/Au(111)		Bz/Cu(111)		Bz/Pt(111)		Bz/Pd(111)		Bz/Rh(111)		Bz/Ni(111)	
	d_{C-M}	d_{H-M}	d_{C-M}	d_{H-M}	d_{C-M}	d_{H-M}	d_{C-M}	d_{H-M}	d_{C-M}	d_{H-M}	d_{C-M}	d_{H-M}	d_{C-M}	d_{H-M}
PBE	3.55	3.55	3.46	3.46	3.42	3.42	2.14	2.57	2.15	2.50	2.16	2.56	2.07	2.42
optB86b	3.02	3.03	3.03	3.05	2.83	2.85	2.12	2.55	2.13	2.48	2.14	2.54	2.01	2.39
optB88	3.08	3.08	3.08	3.09	2.91	2.92	2.14	2.57	2.16	2.50	2.17	2.56	2.08	2.42
optPBE	3.23	3.23	3.21	3.21	3.14	3.15	2.15	2.58	2.17	2.51	2.18	2.57	2.09	2.43
revPBE	3.51	3.51	3.44	3.44	3.46	3.46	2.19	2.61	2.24	2.55	2.22	2.60	2.16	2.48
rPW86	3.40	3.40	3.31	3.31	3.39	3.39	2.22	2.63	2.31	2.65	2.28	2.63	2.23	2.52
Experiment	-		-		-		2.18[49]		-		-		1.91-1.92[50,51]	

For transition metal substrates, the comparison between adsorption energies calculated using the vdW functionals and PBE reveals an interesting feature, however, somewhat expected. For these substrates, the inclusion of vdW interactions via the opt-type functionals increases significantly the adsorption energies (above an eV) in comparison with PBE results (see Table 3). Systematically, for each surface, the adsorption energies are found to be the highest when the optB86b functional is used. The influence of less "repulsive" nature of the opt-type functionals on the adsorption is evident in the tables. On the other hand, the revPBE and rPW86 functionals lower the adsorption energies, and the reduction from that of PBE is the most significant (400-700 meV) when rPW86 functional is used. Tables 2-3 show systematically larger adsorption heights and lower adsorption energies when the rPW86 is used, revealing its strong repulsive nature at short ranges [41]. A similar trend was reported recently for Benzene on Pt(111) [32].

Table 3. Adsorption energies (in eV) calculated using PBE and vdW functional along with the available experimental data. The adsorption energy is defined as $E_{ads} = - (E_{Bz/surf} - E_{surf} - E_{Bz})$, where the subscripts Bz/surf, surf, and Bz refer to the total energies of benzene on surface, the clean surface, and isolated benzene systems, respectively.

Method	Bz/Ag(111)	Bz/Au(111)	Bz/Cu(111)	Bz/Pt(111)	Bz/Pd(111)	Bz/Rh(111)	Bz/Ni(111)
PBE	0.06	0.06	0.07	1.19	1.19	1.54	0.98
optB86b	0.76	0.86	0.82	2.42	2.36	2.81	2.19
optB88	0.72	0.82	0.74	2.02	2.01	2.40	1.79
optPBE	0.71	0.71	0.68	1.77	1.75	2.21	1.48
revPBE	0.55	0.56	0.53	0.98	1.02	1.33	0.69
rPW86	0.52	0.55	0.49	0.60	0.77	0.90	0.27
Experiment	0.42[52] *0.66-0.80[31]	0.64[53]	0.62[54] *0.68-0.81[31]	1.49-1.83[55]	1.35[56] 1.44-2.04[57]	-	0.78[58]

*A recent interpretation of the temperature-programmed desorption (TPD) for benzene at hcp 30° site using the Redhead formula for the range of pre-exponential factors 10^{15}-10^{18} s^{-1} [31].

A direct comparison of the adsorption energies with available experimental data is non trivial if the energies are extracted using the temperature programmed desorption (TPD), where desorption energies are determined at desorption temperatures. For molecules like benzene, fragmentation may even make it impossible to determine a desorption temperature. On the other hand, calorimetry experiments give a true measure of adsorption energy, the one worth mentioning is the adsorption on Pt(111) [55]. In this experiment, the adsorption energy was extracted for different coverage, and a simple formula was fitted to the following equation: E (in kJ/mol) = 197 - 48θ - 83θ^2. The θ is coverage, with θ =1 corresponding to saturation with an estimated error of 10% for the desorption energy. From the experimental observation, the adsorption energy can vary between 0.68 eV for full coverage and 2.04 eV for zero coverage, a change of 300%. Thus, the experimental adsorption energies (via TPD) should be taken as a lower bound, at best. In the calorimetry experiment [55], the saturation occurs when C/Pt ratio is 6/7, while for our case C/Pt ratio is 6/16. Using θ =7/16, we find the lower and upper limits to be 1.49 eV and 1.83 eV, respectively. Although it is challenging to determine which functional gives the best performance based on scarce experimental data with high uncertainties in the derivation of the adsorption energies, and scattered computed adsorption energies, we attempt hereafter a *tentative* quantitative comparison at which we exclude the adsorption energies on Ni(111). For this system, we suspect that the experimental observation underestimates the adsorption energy although the

corresponding adsorption height is about 1.9 Å. For this exercise, we first determine average experimental adsorption energies whenever an upper and lower bound values are available in Table 3. Note here that for benzene on Au(111), only one value was found. Thus, we have used the following averaged adsorption energies for benzene on Ag, Au, Cu, Pt, and Pd as 0.73eV, 0.64eV, 0.74eV, 1.66eV and 1.70eV, respectively. The percentage changes (from the average experimental values) for the calculated adsorption energies are determined for each case that is reported in Table 3. Our analysis of the comparison made using averaged experimental adsorption energies suggests that the best overall performance corresponds to the results obtained using the optPBE functional. For this functional, the percentage changes in the adsorption energies from those of the experimental values are 3% for Ag and Pd, 6%, 8% and 11% for Pt, Cu and Au, respectively. The results obtained using optB88 functional show the next best variations of 0% for Cu and 1% for Ag, while we find a dramatic increase to 18% for Pd, 22% for Pt, and 28% for Au. The adsorption energies determined using optB86b functional present a relatively good performance for Ag (4%) and Cu (11%), while large variations are obtained for Au (34%), Pd (39%) and Pt (46%). The percentage changes for the revPBE functional, which gives systematically much lower adsorption energies (in particular on transition metal substrates) as compared to the opt-type functionals, are 13%, 25%, 28%, 40%, and 41% for Au, Ag, Cu, Pd, and Pt, respectively. The largest percentage changes are found for the rPW86 functional as 14%, 29%, 34%, 55%, and 64% for Au, Ag, Cu, Pd, and Pt, respectively. In the light of this simple comparison, our observation suggests that optPBE and optB88 functionals show systematically good performance for predicting the adsorption energies within the experimental uncertainties. We should however stress again that this is a rather simple analysis that begs for more experimental studies on the subject.

In Fig. 3.a-b, adsorption energies are plotted as a function of adsorption heights for coinage (see Fig.3.a) and transition metal substrates (see Fig.3.b). As evident from Fig. 3.a, the adsorption heights are the largest for PBE than those of revPBE and rPW86, and the smallest for the opt-type functionals. The substantial reduction obtained using the opt-type functionals can be correlated with the increase in the adsorption energies, particularly for those calculated using optB86b functional. For strongly bound systems

(see Fig.2.b and Fig.3.b), the adsorption is governed both by vdW interactions, and covalent bonding. The adsorption heights calculated using the opt-type functionals are similar to those found using PBE (see Fig.3.b and Table 2); however, the effect of vdW interaction manifests itself as the significant increase in adsorption energies (see Table 3).
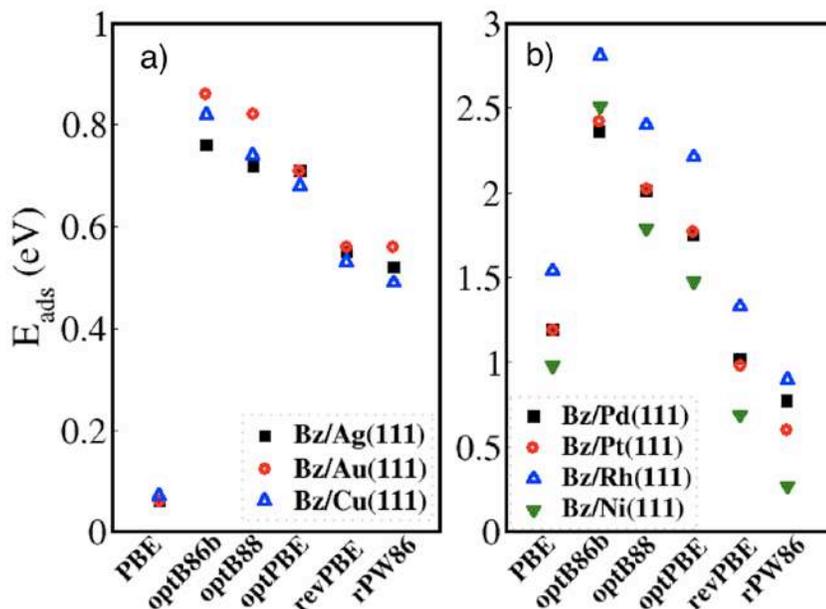

Figure 2. Benzene adsorption energy (E_{ads}) with respect to vdW functionals, and PBE on **a)** coinage substrates and **b)** transition metal substrates.

The most significant trend for the adsorption heights on transition metals is the increase from those of PBE when the revPBE and rPW86 functionals are used (see Fig.3.b). This correlates with the systematic reduction in the adsorption energies obtained in comparison with those using PBE. This trend helps further in *grouping* the contributions from these vdW functionals by simply dividing the plot (Fig. 3.b) into two regions. The solid line in the Fig.3.b separates the adsorption heights calculated using revPBE and rPW86 functionals, which give the largest adsorption heights and the lowest adsorption energies (right side of the solid line in Fig. 3.b) from the opt-type functionals, which give small adsorption heights and the highest adsorption energies (the left side of the solid line). Similar observation is encountered recently for the adsorption of Olympicene radical on Cu(111) [59]. Between these two regions are the PBE results. The reduced adsorption energies and the largest adsorption heights encountered using revPBE and rPW86 functionals indicate their strong repulsive nature at short ranges [41].
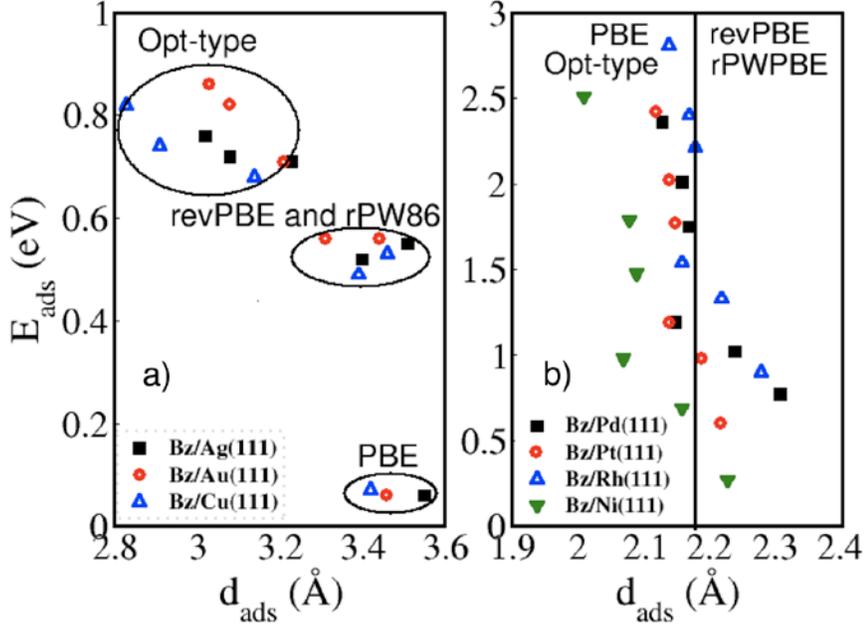
Figure 3. Adsorption energies as a function of adsorption heights (d_{ads}) for **a)** coinage substrates, and **b)** transition metal substrates.

The changes in the surface electronic structure are explored using the changes in the d-band center position and width with varying functionals. We show that the trends in the surface electronic structure obtained using different functionals can also be grouped. The details are presented in the Supplemental Material.

IV. Conclusions

In summary, benzene adsorption characteristics on coinage and transition metal surfaces are studied to explore the role of non-local correlations, and compare the performance of the functionals considered. Adsorption on coinage substrates suggests a systematic increase in adsorption energies with the inclusion of vdW interactions. On transition metals, a significant increase is found when using opt-type functionals in contrast with the reduction obtained using the revPBE and rPW86 functionals from those of PBE. The observations based on the adsorption energy and height relations, and the changes in the surface electronic structure indicate that these functionals can be grouped, and the nature of bonding, in particular, on transition metal substrates can vary dramatically depending on the functional used.

A tentative quantitative comparison between the computed and the experimentally reported adsorption energies suggests that the optPBE and optB88 functionals show a systematic good agreement with "averaged" experimental adsorption energies. This conclusion, however, should be taken with caution as the available experimental data, in general, present large error bars due to the difficulties surrounding the experimental determination of the adsorption energies for such organic systems as those presented here. Taking into account the above-mentioned aspects, we conclude that although the opt-type functionals show promise, these pairwise additive methods neglect the many-body effects. It is clear that adsorption is challenging for dispersion-based DFT methods at present; nevertheless, our results provide comparison for the performance of the current schemes, which is of a broad interest for adsorption studies.

Acknowledgements

[*] Now at Purdue University, School of Chemical Engineering
[+] Corresponding Authors: hyildirim@purdue.edu, Abdelkader.Kara@ucf.edu

References

[1] Sayes, M.; Reyniers, M.-F.; Marin, G.B.; and Neurock, M. *J. Phys. Chem. B* **2002**, *106*, 7489.
[2] Sayes, M.; Reyniers, M.-F.; Neurock, M.; and Marin, G.B. *J. Phys. Chem. B* **2003**, *107*, 3844.
[3] Somorjai, G.A. *Introduction to Surface Chemistry and Catalysis*; Wiley: New York, **1994**.
[4] Tour, J.M.; Jones, L.; Pearson, D.L.; Lamba, J.J.S.; Burgin, T.P.; Whitesides, G.M.; Allara, D.L.; Parikh, A.N.; and Atre, S.V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
[5] Witte, G.; and Wöll, C.J. *J. Mater. Res.* **2004**, *19*, 1889.
[6] Zaera, F. *Chem. Rev.* **1995**, *95*, 2651.
[7] Wolkow, R.A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.
[8] Barlow, S.M.; and Raval, R. *Surf. Sci. Rep.* **2003**, *50,* 201.
[9] Held, G. *J. Phys. Condens. Matter* **2003**, *15*, R1501.
[10] Filler, M.A.; and Bent, S.F. Prog. *Surf. Sci.* **2003**, *73,* 1.
[11] Jenkins, S.J. *Proc. R. Soc. A* **2009***, 465,* 2949.
[12] Vanin, M.; Mortensen, J.J.; Kelkkanen, A.K.; Garcia-Lastra, J.M.; Thygesen, K.S.;

and Jacobsen, K.W. *Phys. Rev. B* **2010**, *81,* 081408.

[13] Toyoda, K.; Hamada, I.; Lee, K.; Yanagisawa, S.; and Morikawa, Y. *J. Chem. Phys.* **2010**, *132,* 134703.

[14] Wellendorff, J.; Kelkkanen, A.; Mortensen, J.J.; Lundqvist, B.I.; and Bligaard, T. *Top. Catal.* **2010**, *53,* 378.

[15] Abad, E.; Dappe, Y.J.; Mart́ınez, J.I.; Flores, F.; and Ortega, J. *J. Chem. Phys.* **2011**, *134,* 044701.

[16] Bilic, A.; Reimers, J.R.; Hush, N.S.; Hoft, R.C.; and Ford, M.J. *J. Chem. Theory Comput.* **2006**, *2,* 1093.

[17] Medeiros, P.V.C.; Gueorguiev, G.K.; and Stafstro̎m, S. *Phys. Rev. B* **2012**, *85,* 205423.

[18] Morin, C.; Simon, D.; and Sautet, P**.** *J. Phys. Chem. B* **2003**, *107,* 2995.

[19] Morin, C.; Simon, D.; and Sautet, P. *J. Phys. Chem. B* **2004**, *108,* 5653.

[20] Orita, H.; and Itoh, N. *Appl. Catal. A: General* **2004**, *258,* 17.

[21] Gao, W.; Zheng, T.;. and Jiang, Q. *J. Phys. Chem.* **2008**, *129,* 164705.

[22] Da Silva, J.L.F.; Stampfl, C.; and Scheffler, M. *Phys. Rev. Lett.* **2003**, *90,* 066104.

[23] Chen, D.L.; Al-Saidi, W.A.; and Johnson, J.K. *Phys. Rev. B* **2011**, *84,* 241405.

[24] Silvestrelli, P.L.; Ambrosetti, A.; Grubisic, S.; and Ancilotto, F. *Phys. Rev. B* **2012**, *85,* 165405.

[25] Dion, M; Rydberg, H; Schro̎der, E; Langreth, D.C.; and Lundqvist, B.I. *Phys. Rev. Lett.* **2004**, *92,* 246401

[26] Tkatchenko, A.; and Scheffler, M. *Phys. Rev. Lett.* **2009**, *102,* 073005.

[27] S. Grimme; J. Antony; S. Ehrlich; and H. Krieg, *J. Chem. Phys.* **2010**, *132,* 154104.

[28] J. Klimeš; D. R. Bowler; and A. Michaelides, *J. Phys. Condens. Matter* **2010**, *22,* 022201.

[29] Tkatchenko, A.; Romaner, L.; Hofmann, O.T.; Zojer, E.; Ambrosch-Draxl, C.; and Scheffler, M. *MRS Bull.* **2010**, *35,* 435.

[30] Carrasco, J.; Santra B.; Klimeš, J.; and Michaelides, A. *Phys. Rev. Lett.* **2011**, *106,* 026101.

[31] Ruiz, V.G.; Liu, W.; Zojer, E.; Scheffler, M.; and Tkatchenko, *Phys. Rev. Lett.* **2012**, *108,* 146103.

[32] Liu, W.; Carrasco, J.; Santra, B.; Michaelides, A.; Scheffler, M.; and Tkatchenko, A. *Phys. Rev. B* **2012**, *86,* 245405.

[33] Perdew, J.P.; Ernzerhof, M.; and Burke, K. *J. Chem. Phys.* **1996**, *105,* 9982.

[34] Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. **1996**, *77,* 3865.

[35] Klimeš, J.; Bowler, D.R.; and Michaelides, A. *Phys. Rev. B* **2011**, *83,* 19513.

[36] Kresse, G.; and Hafner, J. *J. Phys. Rev. B* **1993**, *47,* C558.

[37] Kresse, G.; and Furthmu̎ller, J. *Comput. Mater. Sci.* **1996,** *6*, 15.

[38] Kresse, G.; Furthmüller, *J. Phys. Rev. B.* **1996,** *54*, 11169.

[39] Thonhauser, T.; Cooper, V. R; Li, S.; Puzder, A.; Hyldgaard, P; Langreth, D.C. *Phys. Rev. B,* **2007**, *76*, 125112.

[40] Lee, K.; Murray, E.D; Kong, L.; Lundqvist, B.I.; and Langreth, D.C. *Phys. Rev. B* **2010,** *82,* 081101.

[41] Klimeš, J.; Bowler, D.R.; and Michaelides, A. *J. Chem. Phys.* **2012**, *137,* 120901.

[42] Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59,* 1758.

[43] Blöchl, P. *Phys. Rev. B* **1994**, *50*, 17953.

[44] Monkhorst, H.J.; and Pack, J.D. *Phys. Rev. B* **1976,** *13,* 5188.

[45] Hao, P.; Fang, Y.; Sun, J.; Csonka, G.I; Philipsen, P.H.T.; and Perdew, J.P. *Phys. Rev. B* **2012,** *85,* 014111.

[46] Yamagishi, S.; Jenkins, S.J.; and King, D.A. *J. Chem. Phys.* **2001**, *114,* 5765.

[47] Mittendorfer, F.; Thomazeau, C.; Raybaud, P.; and Toulhoat, H. *J. Phys. Chem. B* **2003**, *107,* 12287.

[48] Gao, W.; Zheng, W.; and Jiang, Q. *J. Chem. Phys.* **2008**, *129,* 164705.

[49] Wander, A.; Held, G.; Hwang, R.Q.; Blackman, G.S.; Xu, M.L.; de Andres, P.; Van Hove, M.A.; and Somorjai, G.A. *Surf. Sci.* **1991**, *249*, 21.

[50] Held, G.; Bessent, M.P.; Titmuss, S.; and King, D.A. *J. Chem. Phys.* **1996**, *105,* 11305.

[51] Schaff, O.; Fernandez, V.; Hofmann, Ph.; Schindler, K.-M; Theobald, A.; Fritzsche, V.; Bradshaw, A.M.; Davis, R.; and Woodruff, D.P *Surf. Sci.* **1996**, *348,* 89.

[52] Zhou, X.-L; Castro, M.E.; and White, J.M. *Surf. Sci.* **1990**, *238,* 215.

[53] Syomin, D.; Kim, J.; Koel, B.E.; and Ellison, G.B. *J. Phys. Chem. B.* **2001**, *105,* 8387.

[54] Xi, M.; Yang, M.X.; Jo, S.K.; Bent, B.E.; and Stevens, P. *J. Chem. Phys.* **1994**, *101,* 9122.

[55] Ihm, H.; Ajo, H. M.; Gottfried, J.M; Bera, P.; and Campbell, C.T. *J. Phys. Chem. B* **2004**, *108,* 14627.

[56] Tysoe, W.T.; Ormerod, R. M.; Lambert, R.M.; Zgrablich, G.; and Ramirez-Cuesta, A. *J. Phys. Chem.* **1993**, *97,* 3365.

[57] Lee, A.F.; Wilson, K.; Lambert, R.M.; Goldoni, A.; Baraldi, A.; and Paolucci, G.; *J. Phys. Chem. B,* **2000**, *104,* 11729.

[58] Myers, A.K.; Schoofs, G.R.; and Benziger, J.B. *J. Phys. Chem.* **1987**, *91*, 2230.

[59] Yildirim, H.; Kara, A. *J. Phys. Chem. C* **2013**, *117,* 2893.