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Density functional study of the adsorption and van der Waals binding of aromatic and conjugated compounds on the basal plane of MoS₂

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Accurate calculations of adsorption energies of cyclic molecules are of key importance in investigations of, e.g., hydrodesulfurization (HDS) catalysis. The present density functional theory (DFT) study of a set of important reactants, products, and inhibitors in HDS catalysis demonstrates that van der Waals interactions are essential for binding energies on MoS₂ surfaces and that DFT with a recently developed exchange-correlation functional (vdW-DF) accurately calculates the van der Waals energy. Values are calculated for the adsorption energies of butadiene, thiophene, benzothiophene, pyridine, quinoline, benzene, and naphthalene on the basal plane of MoS₂, showing good agreement with available experimental data, and the equilibrium geometry is found as flat at a separation of about 3.5 Å for all studied molecules. This adsorption is found to be due to mainly van der Waals interactions. Furthermore, the manifold of adsorption-energy values allows trend analyses to be made, and they are found to have a linear correlation with the number of main atoms. © 2009 American Institute of Physics. [DOI: 10.1063/1.3086040]

I. INTRODUCTION

The strict legislations on sulfur contents in diesel fuel require that the most refractory sulfur containing compounds are removed from the crude oil. This has increased the interest in the reaction mechanisms in hydrodesulfurization (HDS) catalysis in order to improve present day catalysts.[1–6] A key to understanding the reaction mechanisms is the detailed knowledge of the reaction energy landscape. This requires methods to accurately calculate or measure adsorption energies of reactants, products, and inhibitors and barriers of the reactions.

Several earlier density functional theory (DFT) studies of HDS catalysis have elucidated structure, adsorption properties, and reactivity of HDS catalysts.[2–5,7–15] In calculating accurate chemisorption energies of molecules on surfaces, the DFT has a well-proven record.[16] The calculation of physisorption energies has been much more of a challenge, however, due to the absence of the ubiquitous van der Waals (vdW) forces in the most widely used implementations of DFT. The concept "vdW forces" includes forces due to permanent-dipole dipole interactions, permanent-dipole and induced-dipole interactions, and instantaneous induced-dipole induced-dipole interactions, also called London dispersion forces. The most widely used implementations of DFT do not include the nonlocal London dispersion forces. The lack of vdW forces could be problematic in studies of HDS, since most of the molecules of interest in HDS are aromatic. Such molecules are believed to have a considerable part of the binding due to vdW forces. However, recent de-velopments in exchange-correlation (xc) functionals,[17–19] resulting in a novel xc functional (vdW-DF) that accounts for vdW forces, including the London dispersion forces, have shown promising results for adsorption and binding in a variety of systems with significant vdW interactions.[17,20–27]

The adsorption of aromatic (thiophene, benzothiophene, benzene, naphthalene, pyridine, quinoline) and conjugated compounds (butadiene) on the basal plane of MoS₂ is investigated by use of the vdW-DF functional.[17] Thereby, the importance of vdW forces on adsorption energies on MoS₂ is elucidated. The molecules investigated represent both HDS reactants such as thiophene and benzoethiophene and HDS products such as butadiene.[28] Benzene and naphthalene represent weak inhibitors while pyridine and quinoline are much stronger inhibitors of HDS.[12,28,29] It is found that the adsorption of both aromatic and conjugated compounds on the MoS₂ basal plane is dominated by vdW interactions. Results from well defined ultrahigh vacuum surface science experiments[30] on the binding of butadiene and thiophene agree well with the theoretical results, thereby indicating that the vdW interaction for adsorption on MoS₂ based system is well described by the vdW-DF functional. The vdW-DF method uses the exchange functional of the generalized gradient approximation (GGA) flavor revPBE.[31] Here results are also calculated with the RPBE exchange functional[16] which gives essentially the same results (RPBE-vdW).

II. CALCULATIONAL DETAILS

To investigate the basal plane (0001) of MoS₂, a slab model is used. The supercell has four MoS₂ units in the *x*- and *y*-directions and one unit cell in the *z* direction. The slabs are separated by 21.82 Å in the *z*-direction. This model represents the basal plane of MoS₂ single crystal, where the

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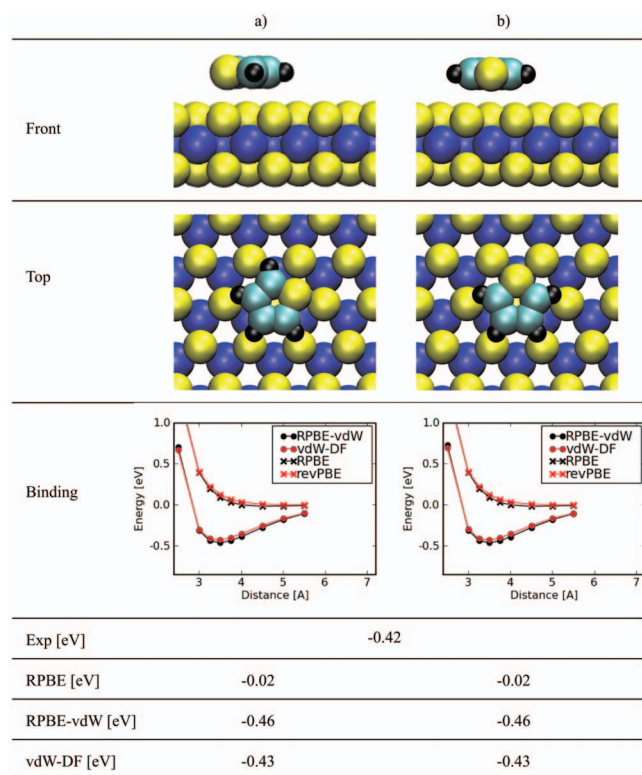
FIG. 1. (Color) Thiophene adsorption. Experimental value is from Ref. 30. Mo atoms are blue (big, dark gray), S atoms yellow (big, light), C atoms light blue (medium-sized, light gray), and H atoms black (small, black).

effect of the second layer of MoS_2 is assumed to be small. This has been shown to be a reasonable approximation for graphite, where addition of a second layer is estimated to give less than 6% increase in the binding between bulk graphite multilayers, i.e., an increase from 48 to 50.5 meV/ atom, when going from the exfoliation energy to the graphite cleavage energy,[21] thus adsorption energies are underestimated by approximately 3% when the multilayer slab is modeled as a single layer. A similar figure (0.01 eV strengthening of the bond) can be extracted from the thiophene adsorption result in Fig. 1.

The plane-wave DFT code DACAPO (Refs. 16 and 32) is used for the self-consistent GGA part of the calculations, the one for the structure optimization. The Brillouin zone is sampled using a Monkhorst–Pack k-point set[33] containing four k-points in the x- and y-directions and one k-point in z-direction. The calculated equilibrium lattice constant of $a = 3.235$ Å compares well to the experimental lattice constant of 3.16 Å.[34] A plane-wave cutoff of 30 Ry and a density cutoff of 60 Ry are employed using the double-grid technique.[35] Ultrasoft pseudopotentials are used except for sulfur, where a soft pseudopotential is employed.[36,37] A Fermi temperature of $k_B T = 0.1$ eV (0.001 eV) is used for slab (molecules) and energies are extrapolated to zero electronic temperature. Figures of atomic structures are made using the computer code VMD.[38] The convergence criterion for the atomic relaxation is that the maximum force on one atom should be smaller than 0.01 eV/Å.

The xc functional RPBE,[16] common in calculations of surface chemistry, is used for structure optimization, as it gives better chemisorption energies for small molecules than other GGA flavors. In the vdW-DF,[17] on the other hand, the GGA flavor revPBE (Ref. 31) is used for the exchange functional. Many standard GGA flavors give an attraction via their exchange functional, a behavior shown to be incorrect by exact exchange calculations. The revPBE exchange functional has been fitted to exact exchange calculations[31] and has less of the mentioned problem, which is why it is used in vdW-DF.[17] The ultimate exchange functional is the exact Hartree–Fock exchange. Use of it instead of revPBE exchange in a vdW-DF calculation for, e.g., dimers of benzene[23] and similar test systems[39] gives improved values for the equilibrium separation values but larger values for the binding energy. It seems to be the rule in the vdW-DF results that vdW bonds in the vdW-DF are found to be a couple of percent too long, and it is gratifying that its cause is known. The same seems to apply for RPBE-vdW.

RPBE has the advantage that it is completely consistent with the derivation of PBE-type functionals,[40] and for the range of density gradients of importance here, it is essentially the same as the revPBE functional.[16] For this reason the problem with attractive behavior of the exchange functional is small also for RPBE, and the commonness of RPBE in surface chemistry calculations has lead us to perform calculations also with RPBE (Ref. 16) replacing revPBE in the vdW-DF functional. We denote these results RPBE-vdW in Figs. 1–3 and in the text.

The potential energy surfaces (PESs) in Figs. 1–3 show that to within the accuracy of DFT, there is an insignificant difference between RPBE-vdW and vdW-DF results, the latter giving only slightly weaker binding (0.03–0.05 eV).

The vdW-DF and RPBE-vdW codes have recently been implemented in the grid based real space projected augmented wave code GPAW.[41] The E_{vdW-DF} and $E_{RPBE-vdW}$ energies are calculated as perturbations to the RPBE result, using the self-consistent RPBE density. The vdW-DF xc energy is given as[17]

$$E_{xc} = E_{LDA,c} + E_{GGA,x} + E_c^{nl},$$

where $E_{LDA,c}$ is the LDA correlation, $E_{GGA,x}$ the GGA exchange energy, equal to $E_{revPBE,x}$ in the vdW-DF functional and to $E_{RBPE,x}$ in RPBE-vdW, according to reasons given above. The nonlocal correlation energy E_c^{nl} is calculated as[17]

$$E_c^{nl} = \frac{1}{2} \int \int n(r)\phi(r,r')n(r')drdr',$$

where the interaction kernel $\phi(r,r')$ is calculated as described in Ref. 17. The integral is evaluated for densities above $0.0001/a_0^3$ and a density grid spacing of 0.10 Å. The periodic boundary conditions are included using the minimum image convention.[42]

The PESs are constructed in the following way. The binding site and orientation of the molecule are determined using DACAPO with the RPBE functional. Two different approaches are used. (i) Simple structure optimization keeping the slab fixed is used for nonparallel adsorption; (ii) for parallel adsorption the z coordinate (z is chosen to be perpendicular to the surface plane) of the molecule is fixed at a distance of 3.5 Å above the surface. A flat adsorption is
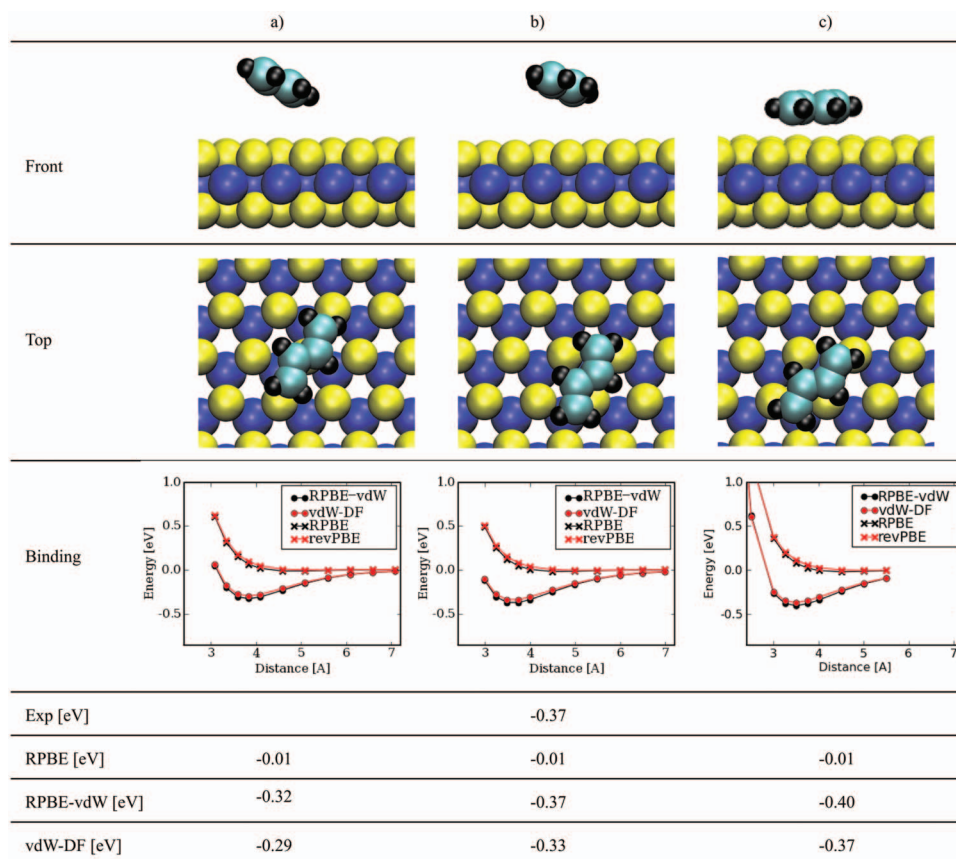
FIG. 2. (Color) Butadiene adsorption on the basal plane of MoS$_2$. The abscissa in the PESs is the distance from the center of mass of butadiene to the z position of the top sulfur layer. Experimental value from Ref. 30. The code for the atoms is the same as in Fig. 1.

	a)	b)	c)
Exp [eV]		-0.37	
RPBE [eV]	-0.01	-0.01	-0.01
RPBE-vdW [eV]	-0.32	-0.37	-0.40
vdW-DF [eV]	-0.29	-0.33	-0.37

thereby ensured and the determination of the optimal orientation of the molecule at distances closer than the RPBE equilibrium distance made possible. Having determined the x and y coordinates of the binding sites, the PES along the z coordinate is calculated by displacing the molecule along the z coordinate. For each displacement four different total energies are calculated: (i) the RPBE total energy calculated using DACAPO with the RPBE xc functional; (ii) the non-self-consistent revPBE total energy calculated using DACAPO and the RPBE density; (iii) the RPBE-vdW total energy using the RPBE exchange energy calculated using DACAPO and the nonlocal correlation energy calculated by GPAW with the RPBE density as input; (iv) the vdW-DF total energy calculated using the revPBE exchange energy calculated by DACAPO and the nonlocal correlation energy calculated by GPAW with the RPBE density as input. The fact that the self-consistent RPBE and revPBE densities are close to each other is thus utilized.

III. RESULTS AND DISCUSSION

The adsorption systems of butadiene, thiophene, dibenzothiophene, pyridine, quinoline, benzene, and naphthalene on the basal (0001) plane of MoS$_2$ are investigated. For the first mentioned ones, thiophene and butadiene, there are previous results from well defined surface science experiments.[30] The binding on the basal plane is found weak, with thiophene and butadiene adsorption-energy values measured as -0.42 and -0.37 eV, respectively.

IV. THIOPHENE

For thiophene, there are two adsorption configurations [(a) and (b) in Fig. 1] with very similar binding energies and PESs. Little or no chemical bonding is found, the entire bond is given by vdW interaction, and the molecule lies flat at about 3.5 Å above the basal plane. The adsorption-energy values calculated in vdW-DF (-0.43 eV) and RPBE-vdW (-0.46 eV) compare well with the experimental number (-0.42 eV).

V. BUTADIENE

Three different butadiene adsorption configurations [(a)–(c) in Fig. 2] have been investigated and the calculated PESs can be seen in Fig. 2. The binding energy values for the different adsorption configurations are very similar, and the maximum vdW-DF (RPBE-vdW) binding is -0.37 eV (-0.4 eV) found for the flat adsorption mode at a separation of 3.5 Å from the basal plane. Like for thiophene, the binding energies are dominated by vdW interactions. The agreement between the experimental and the calculated adsorption-energy values is high.

VI. CYCLIC AND HETEROCYCLIC MOLECULES

A series of cyclic and heterocyclic molecules relevant for HDS catalysis have been investigated (Fig. 3). There exist no detailed experimental investigations of these molecules on the MoS$_2$ basal plane, however. The binding energy is dominated by vdW interactions, like for thiophene and butadiene. The adsorption-energy values and PESs of benzene
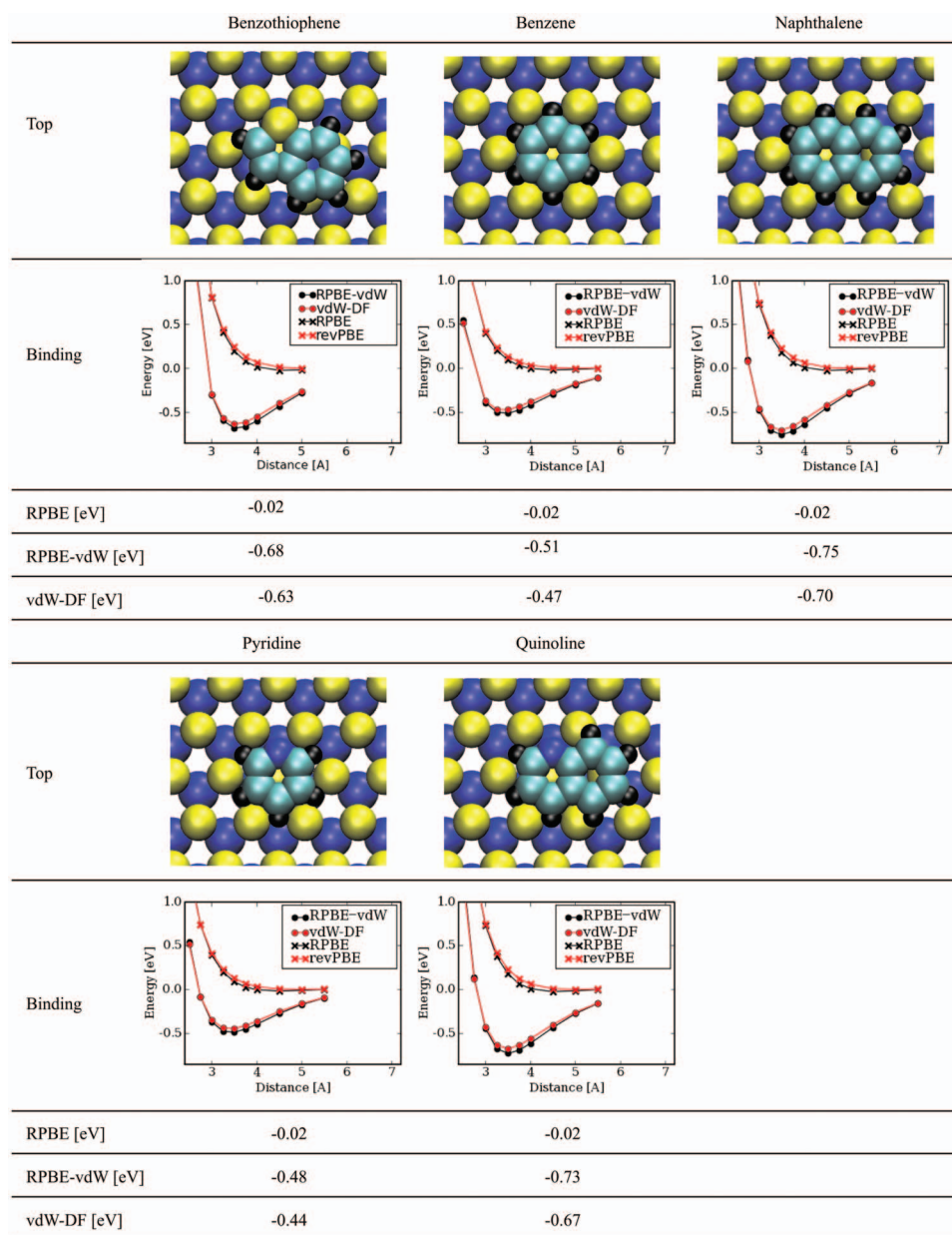
FIG. 3. (Color) Cyclic and heterocyclic adsorption on the basal plane of MoS_2. The abscissa in the PESs is the distance from the center of mass of the molecule to the z position of the top sulfur layer. The color code for the atoms is the same as in Fig. 1.

and naphthalene are very similar on MoS_2 and graphite[21] (adsorption-energy values on graphite being -0.50 eV for benzene and -0.76 eV for naphthalene, respectively, calculated in vdW-DF, that is with revPBE exchange). The parallel geometry is preferred, with the molecular plane about 3.5 Å above the basal plane.

The overall picture is that vdW forces dominate the bonds between the investigated molecules and the basal plane of MoS_2. The equilibrium z-distance from molecule to surface is approximately 3.5 Å for all molecules. In the cases where experimental data are available, i.e., thiophene and butadiene, the experimental values for the adsorption energy agree well with the calculated values.[30] The accuracy of the experimental results is on the level of ± 0.04 for butadiene and ± 0.01 eV for thiophene, thus the present results indicate that the accuracy of the vdW-DF is on the level of ± 0.1 eV, which is similar to the accuracy found for adsorption on graphene.[21] The relatively strong vdW binding energy should relate to the fact that the investigated molecules have delo-

calized electrons in the aromatic structure of the cyclic and heterocyclic molecules and the conjugated double bonds in butadiene. Such electronic states contribute more to the polarization the more delocalized they are. Crudely speaking, the delocalization grows with the number of atoms that are not plainly hydrogen but span up the framework of the molecule.

Figure 4 shows all the calculated adsorption-energy values as functions of the number of main atoms (S, C, N). There is a linear correlation between the number of main atoms and the binding energy. As the density is the key variable in DFT, one possible explanation could be that the density added by each additional main atom is similar and that there is a very small influence by the change in MoS_2 surface density [such an explanation follows trivially from Eq. (2), when the mentioned crude assumptions are made in this equation], something that might be due to the nonlocal nature of the vdW forces. In this connection it is interesting to note that the z-distance from molecule to surface is approxi-
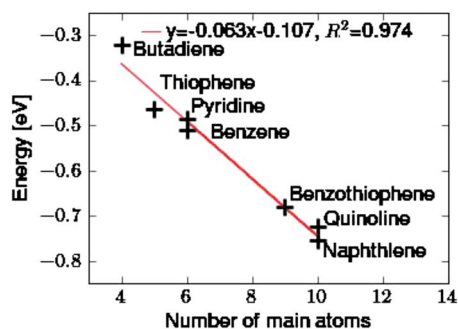
FIG. 4. (Color online) Adsorption energy as a function of the number of main atoms (C,S,N). The straight line is the linear fit to the binding energies.

mately 3.5 Å for all molecules. As all studied molecules adsorb in a flat adsorption mode, with their plane at about 3.5 Å above the surface, the C atoms added to thiophene, pyridine, and benzene have approximately the same z-distance to the surface. It could be speculated that for surfaces with less symmetry, the linear correlation would be less pronounced due to differences in distance to the surface for different parts of the molecule. Another case could be surfaces where chemical bonds are formed which could again remove some of the symmetry.

Correlation between boiling point and molecular weight is well known from experimental studies,[43] thus the vdW-DF xc functional makes it possible to calculate such correlations for extended systems. It is interesting to note that experimental investigation of adsorption of alkanes and cyclic organic molecules in zeolites where vdW forces dominate also finds linear correlations between heats of adsorption and the number of main atoms.[44,45] It is found that the binding energy per atoms due to vdW forces of geometrically hindered molecules is weaker. This indicates that for these molecules planar adsorption on the zeolite walls is not possible and therefore the maximum vdW binding cannot be achieved, similar to what is found presently for nonplaner adsorption of butadiene.

The present results show that vdW binding significantly affects the adsorption energy and thereby the coverage of aromatic compounds on MoS$_2$ based catalysts. Compared to traditional DFT, there is an increase in the adsorption energies by -0.4 eV for butadiene and more for larger molecules. This is of significant importance, since molecules such as thiophene and dibenzoethiophene have been found to make weak chemical bonds with the equilibrium edge structures and single vacancies on the equilibrium edges.[2,5,10,14,15] The linear correlation found in Fig. 4 could be used to estimate the vdW contribution for larger molecules such as dibenzothiophene and could therefore prove to be useful in the development of reaction path diagrams including vdW forces.

VII. CONCLUSION

The adsorption properties of butadiene, thiophene, benzothiophene, benzene, naphthalene, pyridine, and quinoline on the basal plane of MoS$_2$ are calculated with the recently developed xc functional vdW-DF.[17] The adsorption geometries are typically flat with the molecular plane typically 3.5

Å above the basal plane of MoS$_2$. The calculated adsorption-energy values agree very well with available experimental data. For all molecules the bond is found to be due to vdW interactions. The present results for the vdW binding show a magnitude that will influence the coverage of these species considerably.

A simple linear correlation between adsorption-energy values and the number of main atoms is identified. It could be used to determine approximate vdW adsorption energies on MoS$_2$ and should be a challenge for the strive toward a deeper understanding. Obviously, the vdW forces cannot be neglected in calculations of adsorption energies of aromatic and conjugated compounds on inert surfaces, such as the basal plane of MoS$_2$. The high degree of agreement between theory and experiment shows that the vdW-DF functional is promising for accurately calculating adsorption energies.

Needless to say, there are several aspects of the vdW-DF and its application in a context like this that need to be scrutinized, including optimization of the account of exchange, understanding of how seemingly different surfaces, such as graphite and the basal plane of MoS$_2$, can give so similar physisorption values, and the possible coexistence of vdW forces with other forces of a similar magnitude, such as expected covalent ones at, e.g., the edge of nanosized MoS$_2$ triple layers.

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