

Adsorption sites and electronic structure of benzene, naphthalene, and anthracene on a MoS₂ monolayer

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We investigate the adsorption geometry, binding energetics, and electronic structure of the polycyclic aromatic hydrocarbons benzene, naphthalene, and anthracene on a monolayer of MoS₂ using first-principles calculations. Structural relaxations are performed within density functional theory (DFT) including corrections for van der Waals interactions. Quasiparticle electronic structures are subsequently obtained using many-body perturbation theory employing the *GW* approximation. All three molecules preferentially adsorb flat above sulfur sites of the MoS₂ surface and form type-I heterojunctions with MoS₂. Only anthracene exhibits weak hybridization with the MoS₂ valence band maximum (VBM) and VBM-1, leading to a slight reduction of the MoS₂ valence band splitting. The HOMO-LUMO (highest occupied molecular orbital, lowest unoccupied molecular orbital) gaps of the molecules are substantially reduced by the dielectric screening of the MoS₂ substrate. These results highlight the asymmetric role of screening and hybridization in MoS₂-organic hybrid systems and provide insight into band alignment and electronic structure engineering for molecularly functionalized two-dimensional semiconductors.

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I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) such as benzene, naphthalene, and anthracene are prototypical molecules for studying π - π interactions, van der Waals (vdW) binding, charge transfer, and molecular orbital hybridization with solid surfaces [1–4]. These molecules play prominent roles in environmental chemistry (e.g., as pollutants), organic electronics (as components of molecular layers or coatings), and in fundamental surface science (where adsorption, physisorption vs chemisorption, and frontier orbital alignment matter). MoS₂ monolayers are two-dimensional transition metal dichalcogenides (TMDCs) with a direct band gap in the visible to near-infrared range, high chemical stability, and a large exposed surface area [5–7], making them promising substrates for sensing [8–11] and catalysis [12,13], and promising components in (opto-)electronic devices [14–16]. Understanding how PAHs adsorb on MoS₂ and how their presence perturbs the electronic structure of the combined system is therefore of fundamental interest, e.g., to reveal how molecular adsorbates interact with two-dimensional (2D) semiconductors, how screening and vdW interactions modify frontier molecular states, and how band edges shift.

Earlier works have examined benzene adsorbed on MoS₂ monolayers in contexts such as many-body response and vdW interactions, revealing that not only binding energies but also spectral broadening and nonadditive correlations are relevant. For example, Umerbekova *et al.* studied the many-body re-

sponse of benzene on MoS₂, isolating the vdW interaction contribution and examining how adsorption site and distance influence spectral properties [17]. Moreover, in hydrocarbon adsorption under reaction conditions (e.g., naphthalene on MoS₂ in diesel hydrotreating catalyst models), PAHs have been found to be among the strongest adsorbates in terms of adsorption capacity, implying that their adsorption behavior controls the occupation of active sites under realistic conditions [18].

To model these systems accurately, one needs to capture both geometric relaxations under weak vdW forces and the many-body effects governing quasiparticle energy levels for accurate band gaps, molecular HOMO-LUMO (highest occupied molecular orbital, lowest unoccupied molecular orbital) levels, and screening effects. In this work, we combine density functional theory (DFT) using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [19] augmented by Grimme's D3 dispersion correction (PBE-D3) [20] for structural relaxations of the adsorbed molecules on a MoS₂ monolayer, with subsequent calculation of quasiparticle band structures using many-body perturbation theory employing the *GW* approximation. As proposed by Rohlfing [21], we employ the simplified GdW(LDA) approach in which we approximate the self-energy using the difference of the screened Colom interaction *dW* on-top of a DFT-LDA (local-density approximation) calculation (see Sec. II B). The PBE-D3 relaxations ensure that the weak vdW binding and geometric distortions of the molecules are treated reasonably, while GdW(LDA) provides improved quantitative accuracy for the positions of molecular states, band edges, and the adsorption-induced renormalization of those, over pure DFT. Indeed, GdW(LDA) has been used in related work on functionalizing MoS₂ (e.g., with molecular species), where the quasiparticle band gap of MoS₂ in the monolayer increased substantially relative to LDA, and molecular state energies shift due to screening and hybridization [5,22,23].

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In this study, we examine benzene, naphthalene, and anthracene adsorbed on an ideal MoS₂ monolayer. We address several questions: What are the preferred adsorption geometries and associated binding energies? How do the molecular frontier orbitals align relative to the MoS₂ band edges? How does the presence of the molecule modify the quasiparticle band structure of MoS₂? And how significant are screening, hybridization, and vdW effects in determining these features? We intend that our results will be relevant not only for basic science, but also for applications in molecular sensing, surface functionalization, heterojunction device design, and controlling interfacial charge transfer in hybrid MoS₂-organic systems.

II. THEORY

In this section, we briefly explain the theoretical framework how we calculate the electronic structure of MoS₂, hydrocarbon molecules and the composed adsorbate systems. In order to achieve a realistic description of a band structure or of molecular energy states, first the geometry has to be determined, and second the quasiparticle electronic structure has to be derived. For both the geometry and the electronic structure we use our own code.

A. Structural relaxation and binding energy

As the electronic structure strongly depends on the geometry of the investigated system, structural relaxations are carried out to get reliable geometries. Therefore, we perform *ab initio* ground-state DFT calculations based on the generalized gradient approximation (GGA) with the PBE functional [19] including vdW corrections (PBE-D3) [20]. We work with our own DFT code and employ norm-conserving pseudopotentials [24–26] and a basis of atom-centered Gaussian orbitals [27]. This basis consists of three shells per atom, each containing ten basis functions. A shell is defined by a common decay constant of the Gaussians which are listed in Table SI in the Supplemental Material [28] (see also Refs. [19,20,29] therein). Thus, all basis functions within a shell exhibit the same radial decay. The basis functions within a shell have the symmetries s , p_x , p_y , p_z , d_{zx} , d_{yz} , d_{xy} , $d_{3z^2-r^2}$, $d_{x^2-y^2}$, and $s^* = r^2 \times s$ such that we use a total of 30 basis functions per atom. The quality of the basis is comparable at least to a triple-zeta basis.

In the case of adsorbed molecules on the MoS₂ monolayer, the structural relaxations are performed for different initial configurations in order to determine the most strongly bound structure the molecule can take on top of the monolayer. To this end, we investigate one molecule above a MoS₂ supercell, whose size depends on the molecule and, like the height of the corresponding supercell, is carefully chosen such that the interaction between molecules in adjacent supercells is negligible. We have to take the basis set superposition error (BSSE) into account, since our DFT program works with localized Gaussian orbitals that can artificially optimize the wave function of electrons localized at other atoms and that can therefore lead to an artificially decreased total energy. The BSSE is corrected by a counterpoise correction [30] and can be approximated for two systems A and B with bases

a and b as

$$\Delta_{ab,a}^{\text{BSSE}}(A) = E_a(A) - E_{ab}(A). \quad (1)$$

It expresses the effect of the additional basis (here basis b) on the system (here system A). Since we investigate the relaxation process of these systems in addition, we also have to include the corresponding relaxation energy

$$E_{\text{rel}} = E_a(A) - E_{\tilde{a}}(\tilde{A}) + E_b(B) - E_{\tilde{b}}(\tilde{B}), \quad (2)$$

where $\tilde{A}$, $\tilde{B}$ and $\tilde{a}$, $\tilde{b}$ are the isolated structures and associated bases of A and B. The final binding energy of the two systems A and B then reads

$$E_b = E_{ab}(AB) - E_a(A) - E_b(B) + \Delta_{ab,a}^{\text{BSSE}}(A) + \Delta_{ab,b}^{\text{BSSE}}(B) + E_{\text{rel}}. \quad (3)$$

B. Electronic structure

1. GdW(LDA) method

The evaluation of the electronic structure is based on the DFT geometries but is done by the *GW* approach [31] within the GdW(LDA) approximation, which is described briefly in the following. A more detailed derivation is given in [21].

Within the *GW* approach, the quasiparticle Hamiltonian can be written as

$$\hat{H}^{\text{QP}} = \hat{H}^{\text{DFT}} + i\text{GW} - V_{\text{xc}} \quad (4)$$

with the one-particle Green's function G , the screened Coulomb potential W , and the exchange-correlation potential V_{xc} used in the underlying DFT calculation. Although it is possible in principle to calculate a self-consistent solution (G depends on the quasiparticle wave function) for the resulting Schrödinger equation, this is often not necessary to obtain realistic band structures. A non-self-consistent solution is sufficient for this purpose in many cases, but even calculating such a solution can be very time consuming and therefore impractical for large (adsorbate) systems. Within the GdW(LDA) framework, the fundamental DFT calculation is performed within the local density approximation (LDA) [32] and the exchange-correlation potential $V_{\text{xc}} \approx i\text{GW}_{\text{metal}}$ is replaced by the product between the one-particle Green's function and a fictitious metallic screened Coulomb potential W_{metal} . This approximation is justified by the observation that in many systems a *GW* calculation with a hypothetical metallic screening reproduces the LDA band structure with surprisingly good accuracy [33–35]. The expression for the quasiparticle band structure then reads

$$E_{n,\vec{k}}^{\text{QP}} = E_{n,\vec{k}}^{\text{LDA}} + \langle \psi_{n,\vec{k}}^{\text{LDA}} | iG(W - W_{\text{metal}}) | \psi_{n,\vec{k}}^{\text{LDA}} \rangle, \quad (5)$$

so we have to evaluate the difference between two screened Coulomb potentials. This is where the name of the GdW method comes from because instead of a Coulomb potential the difference $W - W_{\text{metal}} = dW$, which is usually a small quantity, has to be considered. As a further approximation, the dielectric model function

$$\varepsilon_{\vec{G},\vec{G}'}(\vec{q}) = \delta_{\vec{G},\vec{G}'} + \frac{1}{|\vec{q} + \vec{G}|} \frac{1}{|\vec{q} + \vec{G}'|} \sum_{j=1}^N \frac{V^{(j)}}{V} \chi_{\vec{G},\vec{G}'}^{(j)}(\vec{q}) \quad (6)$$

that can describe the screened Coulomb potential of both the real and the hypothetical metallic systems, is introduced.

On the one hand this lowers the computational costs drastically because we do not have to calculate the dielectric function in the random phase approximation (RPA), and on the other hand it allows us to calculate the difference of the two screened Coulomb potentials W and W_{metal} very efficiently because both quantities can be evaluated with the same numerical specifications. In this model, $V^{(j)}/V$ denotes the ratio between the volume of the j th atom and the volume of the unit cell (in the bulk), and $\chi^{(j)}$ denotes the static atomic charge density response of that atom, which is located at position $\vec{r}_j$. For the latter, Rohlffing [21] proposed the expressions for the nonmetallic response (used in W),

$$\chi_{\vec{G},\vec{G}'}^{(j)} = \sum_{k=1}^3 \sqrt{f(|\vec{q} + \vec{G}|, \vec{\rho}_j, \varepsilon_j^{(k)}) f(|\vec{q} + \vec{G}'|, \vec{\rho}_j, \varepsilon_j^{(k)})} \times [(\vec{q} + \vec{G}) \cdot \vec{n}_j^{(k)}][(\vec{q} + \vec{G}') \cdot \vec{n}_j^{(k)}] e^{-\gamma_j(\vec{G} - \vec{G}')^2} e^{i(\vec{G}' - \vec{G}) \cdot \vec{r}_j}, \quad (7)$$

and for the metallic response (used for W_{metal}),

$$\chi_{\vec{G},\vec{G}'}^{(j)} = \sqrt{f(|\vec{q} + \vec{G}|, \vec{\rho}_j, \infty) f(|\vec{q} + \vec{G}'|, \vec{\rho}_j, \infty)} \times |\vec{q} + \vec{G}| |\vec{q} + \vec{G}'| e^{-\gamma_j(\vec{G}' - \vec{G})^2} e^{i(\vec{G}' - \vec{G}) \cdot \vec{r}_j}, \quad (8)$$

where the charge-density response (of a homogeneous system) is formulated according to Bechstedt *et al.* [36] such that

$$f(Q, \vec{\rho}, \varepsilon_\infty) = \left(\frac{1}{\varepsilon_\infty - 1} + \frac{Q^2}{q_{\text{TF}}^2(\vec{\rho})} + \frac{Q^4}{\omega_p^2(\vec{\rho})} \right)^{-1}. \quad (9)$$

The model parameters are taken from our *ab initio* calculations. Starting with the average electron density $\bar{\rho} = N_j/V^{(j)}$, where N_j is the number of valence electrons and $V^{(j)}$ is again the volume of the j th atom within the unit cell, the Thomas-Fermi wave number $q_{\text{TF}} = 2\sqrt{3\bar{\rho}\pi}^{-1}$ and the plasma frequency $\omega_p = \sqrt{16\pi\bar{\rho}}$ (both in atomic units) follow directly. The spatial extent γ_j can be determined from least-squares fitting of the atomic charge density by a Gaussian function. We would like to emphasize that the GdW(LDA) method is insensitive to the actual choice of N_j , $V^{(j)}$, and γ_j as the quasiparticle correction depends on the difference of metallic and nonmetallic screening. To incorporate anisotropy, the dielectric constant ε_∞ in f is replaced by a direction-dependent dielectric constant $\varepsilon_j^{(k)}$, and the directions $\vec{q} + \vec{G}^{(v)}$ are projected onto the corresponding principle axes $\vec{n}_j^{(k)}$. This is simplified in metallic systems, where the dielectric constant is isotropic and is ∞ . A more detailed derivation and a comprehensive discussion of the validity of the generalizations made in this model can be found in [21] while an application to TMDCs is given in [5]. The dielectric constants and the principle axes follow from the electric dipole operator for interband transitions,

$$\varepsilon_{a,b} = \delta_{a,b} + \sum_{\vec{k}} \sum_v^{\text{occ}} \sum_c^{\text{emp}} \frac{\langle v\vec{k} | \hat{p}_a | c\vec{k} \rangle \langle v\vec{k} | \hat{p}_b | c\vec{k} \rangle^*}{(E_{c\vec{k}} - E_{v\vec{k}})^3} \quad (10)$$

for $(a, b) \in (x, y, z)$. Using a localized basis, the dielectric screening can be split into atomic ratios; thus we can handle

the anisotropy of a material and we can consider an additional screening from atoms, molecules, etc. that are not part of the currently investigated system by including their $\varepsilon_{a,b}$ calculated in the subsystem. Hence, we can separate the screening and hybridization effects and analyze them independently.

The GdW(LDA) method may not always reach the accuracy of ~ 0.1 eV that is commonly expected from a *GW* calculation, when calculating absolute energies due to its approximations. However, it does allow for the precise calculation of relative energies. We offer some comparisons with other many-body perturbation theory (MBPT) results in Sec. III.

2. Scissor shift

Within the framework of the GdW(LDA) approximation, screened Coulomb potentials $W_{(\text{metal})}$ need to be evaluated, which is typically done by a convolution of the bare Coulomb interaction and the inverse dielectric function. The model function that has been introduced in Eqs. (6) to (8), depends on the DFT band gap through the dielectric model parameters, which allows the application of a supporting scissor shift ΔE . This drives the opening of the gap by shifting all conduction bands by $\Delta\Sigma$, thus $E_{\text{gap}}^{\text{DFT}} \rightarrow E_{\text{gap}}^{\text{DFT}} + \Delta\Sigma$. GdW(LDA) remains an *ab initio* theory as long as the scissor shift is determined in a self-consistent manner, i.e., $E_{\text{gap}}^{\text{GdW(LDA)}} = E_{\text{gap}}^{\text{LDA}} + \Delta E$.

III. RESULTS

We begin with an introduction of the individual systems MoS₂, benzene, naphthalene, and anthracene and discuss their structural as well as electronic properties. Based on that, we discuss the different adsorption sites of the molecules on a MoS₂ monolayer and analyze how the molecule and the MoS₂ affect each other. Further information, such as the convergence behavior of the systems studied with regard to the DFT and GdW(LDA) parameters, and other stable adsorbate configurations that were not analyzed further due to their weaker binding, is provided in the Supplemental material [28].

A. Individual systems

1. Molybdenum disulfide

Molybdenum disulfide (MoS₂) is a layered vdW material [37] and is classified as a TMDC [38]. It has three different (meta)stable crystalline phases (1T, 1T', 2H) as single, exfoliated layers, each with distinct electronic and optical properties. For example, 1T is metallic while 2H is semiconducting [38,39]. We here focus on the 2H structure, which is shown in Fig. 1. The structural relaxation was performed by using PBE because this will be also used in Sec. III B for determining the optimal adsorption site of the investigated acene on the MoS₂ monolayer. The hexagonal unit cell contains one molybdenum and two sulfur atoms. We determined that the lattice constant is $a = 3.20$ Å and the S-S distance is $d_{\text{S-S}} = 3.17$ Å which is comparable to other *ab initio* calculations [6,40–44] and experimental results [45–47]. We analyzed the electronic structure of that PBE geometry by first calculating the LDA band structure, which then was corrected within the framework of GdW(LDA) in order to include quasiparticle

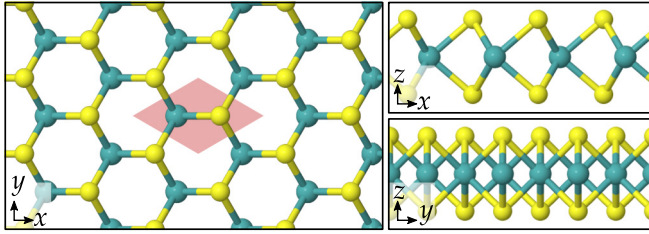


FIG. 1. Atomic structure of a MoS₂ monolayer when looking onto the *xy* plane (left), the *xz* plane (top right), and the *yz* plane (bottom right). The primitive unit cell is marked by the red area and contains one molybdenum atom (blue-green) and two sulfur atoms (yellow).

effects. Both band structures consider spin-orbit coupling and are illustrated in Fig. 2. A list of the fundamental quantities of these band structures is given in Table I and reveals that DFT leads to a much smaller direct band gap than GdW(LDA), which has a more realistic direct band gap of 2.72 eV. The gap opening we can observe was also found by other groups, e.g., by Liang *et al.* [48] (2.75 eV), Ramasubramaniam [42] (2.82 eV) (both on the G_0W_0 level), and Cheiwchanchamnang and Lambrecht [49] (2.759 eV) on the GW level, but is approximately 200 meV lower than the band gap that we calculated earlier in our group (cf. [5]) since we used a PBE structure and not a LDA structure here. The gap was promoted by an extrapolation of band structure calculations of unit cells in cells with different expansions in the *z* direction. This is shown in the inset in Fig. 2. As the Coulomb interaction between periodically repeated unit cells decreases with r^{-1} , the extrapolation for an infinitely extended cell gives the band gap of a simple monolayer in an infinite amount of vacuum. The band splitting of the valence and conduction band at

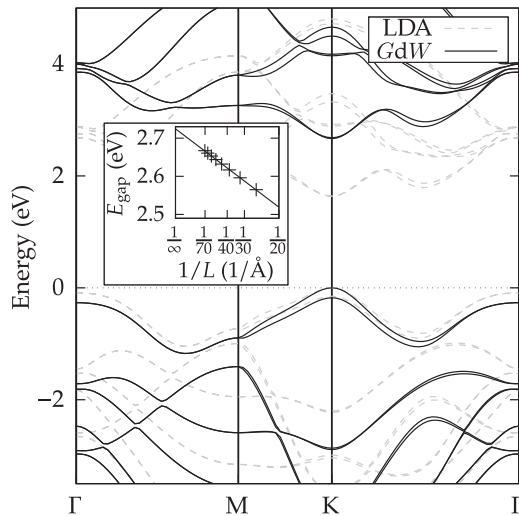


FIG. 2. A comparison of the free-standing MoS₂ monolayer LDA band structure with the GdW(LDA) band structure. The valence band maximum (VBM) is set to 0 eV for better comparability, and the direct band gap is at K. The inset shows the band gap for different cell heights L and the resulting linear extrapolation for an infinitely high cell. The band structures shown are taken from the calculation preformed in the 70 Å high cell.

TABLE I. Band gap (E_{gap}) and band splitting in the valence and conduction band (ΔE_{VB} and ΔE_{CB}) of the MoS₂ monolayer band structure within LDA and GdW(LDA), in an infinite amount of vacuum.

	E_{gap} (eV)	ΔE_{VB} (meV)	ΔE_{CB} (meV)
LDA	1.68	150	3
GdW(LDA)	2.72	178	16

the direct band gap results from the spin-orbit coupling and is pretty strong, as it is for all TMDCs due to the heavy transition metal. It is an important quantity of TMDCs because it can be exploited for spin-selective excitations in optics [50], for instance, and needs to be calculated precisely. The splitting occurs in both LDA and GdW(LDA) but is much smaller in the former. In both approximations, it is more prominent in the valence band than in the conduction band, a finding that has also been observed in other studies, e.g., in [49,51]. Unlike the band gap, the splitting in the valence band and the conduction band is mostly independent of the cell height since it varies less than 0.5 meV in our calculations with cells of height 16 to 70 Å. This change is smaller than the accuracy we can achieve with our GdW(LDA) method, so we conclude that the splitting is already converged for a finite cell height.

2. Benzene, naphthalene, and anthracene

Benzene is a small hydrocarbon with six carbon and six hydrogen atoms that forms a fully hydrogen saturated, planar, hexagonal carbon ring. It is the basic building block for all PAHs, for example naphthalene and anthracene, which consist of linearly in-plane fused benzene rings. The geometries of these three investigated molecules have been calculated in a hexagonal ($32 \times 32 \times 32$) Å³ cell and are shown in Fig. 3. Due to the D_{6h} (benzene) and D_{2h} symmetry, a few bonds share the same length. The calculated bond distances that we get from PBE-D3 calculations are given in Table II. They are in agreement, to within a few picometers, with other experimental and theoretical examinations [52–57], some of which we have listed explicitly in the table. The D3 correction we took into account is negligible compared to a calculation without the D3 correction, and is of minor importance for the isolated molecules because the covalent bonds are much stronger than the vdW interactions. However, we took it into account for reasons of consistency because we have to

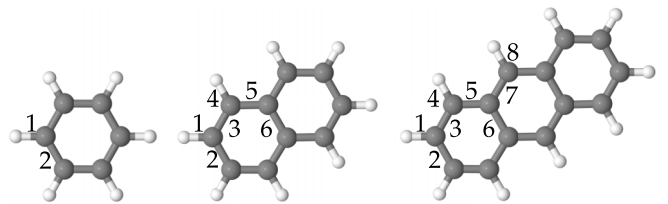


FIG. 3. Structure of benzene (left), naphthalene (middle), and anthracene (right) in their gas phase. The characteristic bonds that fully describe the molecule are numbered here and characterized in Table II.

TABLE II. Type and length of the bonds of the analyzed molecules from Fig. 3. The first value of each bond originates from this work and was calculated using DFT-D3.

	No.	Type	d (Å)	Method	Ref.
Benzene	1	C-H	1.092	DFT	This work
			1.0817	HF+MP2	[52]
			1.08093	Semi-expt. ^a	[54]
	2	C-C	1.398	DFT	This work
			1.3969	HF+MP2	[52]
			1.39134	Semi-expt. ^a	[54]
Naphthalene	1	C-H	1.092	DFT	This work
			1.0829	HF+MP2	[52]
	2	C-C	1.416	DFT	This work
			1.4142	HF+MP2	[52]
			1.417	Experiment ^b	[57]
	3	C-C	1.378	DFT	This work
			1.3791	HF+MP2	[52]
			1.381	Experiment ^b	[57]
	4	C-H	1.093	DFT	This work
			1.0844	HF+MP2	[52]
	5	C-C	1.420	DFT	This work
			1.4187	HF+MP2	[52]
1.422			Experiment ^b	[57]	
6	C-C	1.437	DFT	This work	
		1.4321	HF+MP2	[52]	
		1.412	Experiment ^b	[57]	
Anthracene	1	C-H	1.092	DFT	This work
			1.085	Experiment ^b	[53]
	2	C-C	1.423	DFT	This work
			1.422	Experiment ^b	[53]
	3	C-C	1.372	DFT	This work
			1.397	Experiment ^b	[53]
	4	C-H	1.093	DFT	This work
			1.085	Experiment ^b	[53]
	5	C-C	1.428	DFT	This work
			1.437	Experiment ^b	[53]
	6	C-C	1.449	DFT	This work
			1.437	Experiment ^b	[53]
	7	C-C	1.401	DFT	This work
			1.392	Experiment ^b	[53]
	8	C-H	1.094	DFT	This work
			1.085	Experiment ^b	[53]

^aCombination of Fourier-transform microwave spectroscopy, rotationally resolved IR, UV/vis and Raman spectroscopy, high resolution IR spectroscopy + theoretical corrections of experimental rotation constants.

^bGas electron diffraction.

include the vdW interaction in Sec. III B to determine the most strongly bound adsorption sites.

The energy levels were calculated within LDA and GdW(LDA), which leads to more realistic results than the simple DFT approach. We performed these calculations in hexagonal ($16 \times 16 \times 32$) Å³, ($19.2 \times 19.2 \times 32$) Å³, and ($22.4 \times 22.4 \times 32$) Å³ cells for benzene, naphthalene, and anthracene, respectively. The sizes of the cells ensured that molecules in neighboring cells were not closer than 11 Å apart, thereby significantly reducing the long-ranged Coulomb interaction. The LDA HOMO-LUMO gaps are 5.10,

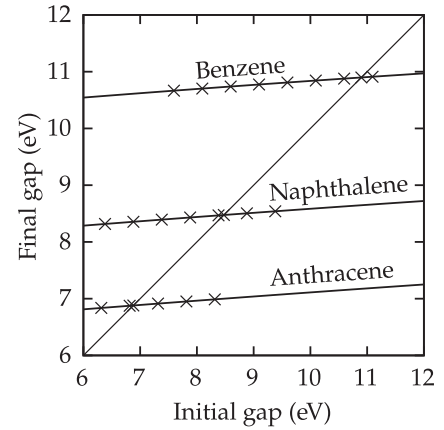


FIG. 4. Determination of the HOMO-LUMO gap of benzene, naphthalene, and anthracene. A self-consistent scissor shift is defined by the intersection of the bisecting line (solid) and the respective fit functions $f(x) = a/(x - b) + c$ (dashed). “Initial gap” refers to the DFT gap enlarged by the scissor shift and “final gap” refers to the resulting GdW(LDA) gap.

3.38, and 2.32 eV for benzene, naphthalene, and anthracene and are drastically underestimated. An opening of the gaps is realized by the GdW(LDA) method and a self-consistent scissor shift (cf. fig. 4) that supports the opening even further. Ultimately, we get HOMO-LUMO gaps of 10.90, 8.48, and 6.88 eV for benzene, naphthalene, and anthracene. These results agree with 10.56 eV (G_0W_0 [58]) and 10.57 eV (expt. [59–61]) for benzene; 7.98 eV (GW [62]) and 8.34 eV (expt. [63]) for naphthalene; and 7.06 eV (GW [64]) and 6.91 eV (expt. [63]) for anthracene.

B. Adsorption sites

In order to determine the optimal adsorption site of each molecule, structural relaxations were performed and the occurring BSSE was corrected. The relaxation was carried out for a single molecule on different MoS₂ supercells with a supercell height of 32 Å. The supercell size was determined such that the wave functions of molecules in adjacent supercells do not overlap. We focus on the case of molecules lying flat on the monolayer with one of the outermost carbon rings centered above the Mo atom, the S atom, the Mo-S bond, and the hollow site of the honeycomb structure, each with different rotations. We neglect possible metastable standing molecule configurations after carefully testing such structures for the case of benzene on the MoS₂ monolayer and noticing that these do not lead to a stable structure. The structure of the MoS₂ substrate is identical to the one we showed earlier in Fig. 1 because we can assume that the strong covalent bonds defining the MoS₂ structure are hardly affected, as the vdW interactions arising from the molecules are significantly weaker. Just the molecules above the monolayer were relaxed until they reached a stable geometry. In the Supplemental Material [28], we present the three configurations that are bound the strongest in Fig. S6 and list their binding energies in Table SII. It can be deduced from this that the most strongly bound configurations of benzene, naphthalene, and anthracene on a MoS₂ supercell are 84, 57, and 31 meV

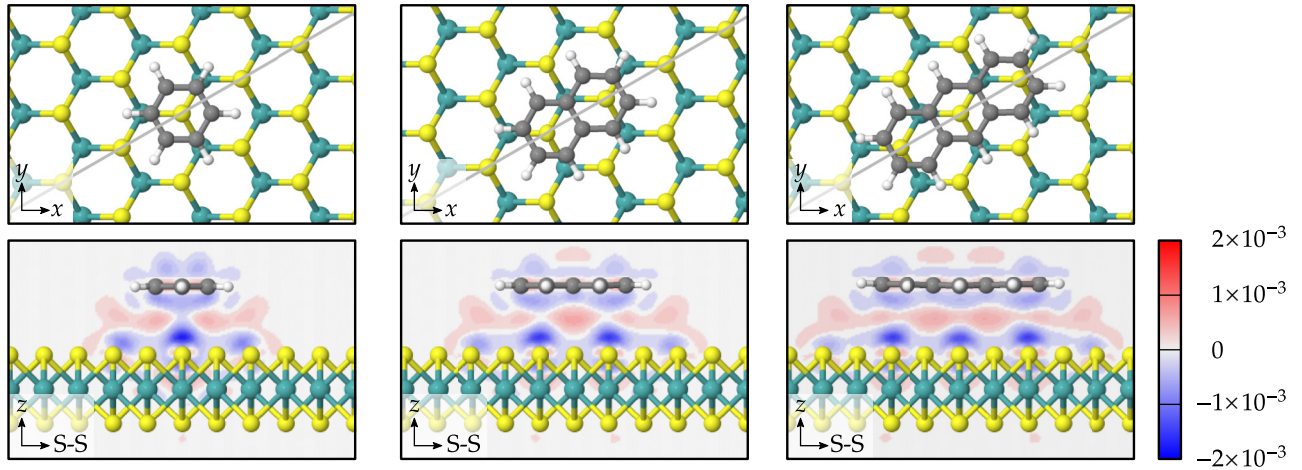


FIG. 5. The most strongly bound adsorption sites for benzene (left), naphthalene (middle), and anthracene (right) on 5×5 , 6×6 , and 7×7 MoS₂ monolayer supercells, respectively. These geometries have been determined by a structural relaxation and a following correction of the height of the molecules, which is evaluated in Fig. 6. The upper panels exhibit how the molecules arrange along the S-S direction of the underlying monolayer. The lower panels show the geometries along the S-S direction and the change in the particle density ($\Delta\rho = \rho_{\text{adsorbate system}} - \rho_{\text{MoS}_2 \text{ supercell}} - \rho_{\text{molecule}}$) on a cross-sectional plane indicated by the light gray line in the upper figure, in units of a_0^{-3} . The color map on the very right is used for all three lower panels. Red (blue) indicate an increase (depletion) of electron particle density.

more strongly bound than the respective second-strongest configurations. Based on this structural relaxations, we gave special attention to the height of the molecule above the substrate of the most strongly bound configuration of each molecule, because a usual structural relaxation often leads to too small distances between molecule and substrate due to the BSSE. The most strongly bound configurations that we were able to identify in this way are characterized by the carbon rings of benzene, naphthalene, and anthracene being located above the S atoms of the substrate. Similar structures have been identified in several publications [1,65–67] each using a plane-wave basis. A more detailed comparison with these references follows at the end this section. As a perfect centering of all carbon rings over S atoms is not possible for naphthalene and anthracene, they align along the S-S direction of the monolayer underneath and marginally increase some of their C-C bonds. The changes in the geometries are small and can be attributed to the discrepancy between the carbon ring size and the MoS₂ honeycomb size because the benzene molecule that can align its center of mass over a S atom does not change its geometry. Figure 5 shows the just described optimal adsorption site for each molecule with the corrected distance between the molecule and the MoS₂ monolayer, and moreover how the electron particle density is affected ($\Delta\rho$) in a symmetry plane of the molecule (gray line). The scale on which the particle density changes in the adsorbate system compared to that of the two individual subsystems is quite small, emphasizing that bonding primarily results from the vdW forces and that no covalent bonds are formed, which would be accompanied by a larger electron transfer and thus a more significant change in particle density. However, it increases within the molecule plane and therefore decreases right above and below the molecules. Between the molecule and the MoS₂ substrate, another area with increased electron particle density forms. The results of the previously men-

tioned height corrections are shown in Fig. 6. To this end, the intramolecular structure was kept fixed but the molecule was vertically displaced, and the corresponding binding energies were interpolated by a quadratic function to determine a local minimum in the binding energy. This approach is justified because the investigated molecules are parallel to the substrate and do not show a significant curvature that might be affected by a different height relative to the substrate. The binding energies (per C atom) and the average height of the molecules are listed in Table III. The correction results in a distance between benzene and the MoS₂ monolayer that is 0.09 Å greater, and a distance between naphthalene and anthracene and the MoS₂ monolayer that is 0.06 Å greater than in the

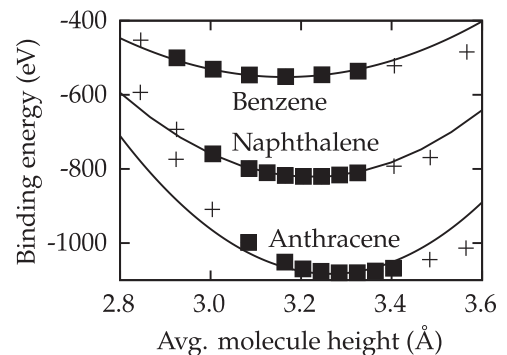


FIG. 6. The distance between molecule and substrate was corrected due to the BSSE. To this end, the binding energy of each molecule for different average heights is interpolated by a quadratic function to determine the minimal binding energy E_b and the optimal average height $\bar{h}$. These results are listed in Table III. The exploited data points for the fit are depicted as solid squares while the remaining data points, for which a quadratic approximation is not justified, are shown as crosses.

TABLE III. The total binding energy E_b (meV), the binding energy per C atom, and the average height $\bar{h}$ (Å) of the molecule above the upper S layer of the MoS₂ substrate.

	E_b	$E_b/\text{C atom}$	$\bar{h}$
Benzene	-551	-92	3.16
Naphthalene	-820	-82	3.22
Anthracene	-1082	-77	3.26

structure optimization performed previously. As noted above, the insufficient height results from the BSSE. These small corrections further reduce the binding energy by 3 to 11 meV. We find that the larger the molecule is, the further away from the MoS₂ monolayer is the stable adsorption configuration and the less its C atoms are bound to it. Compared to benzene, the naphthalene molecule is $\sim 11\%$ and the anthracene molecules is $\sim 16\%$ less strongly bound per C atom. This behavior is in agreement with the vdW interaction between molecule and substrate, which is the main contribution to the binding and which depends reciprocally on the distance.

Rangarajan and Mavrikakis [66] also determined that a fully relaxed benzene molecule is centered over the S atom, and tested this with six DFT methods that account for dispersion interactions. These resulted in binding heights between 3.15 and 3.44 Å, i.e., slightly higher values in average compared to our binding height. The discrepancies can be attributed to the choice of functionals since their PBE-D3 calculation yielded a binding height of 3.15 Å, which differs by 0.01 Å from our PBE-D3 result. They also investigated the binding energy which varies from -0.72 to -0.55 eV, and once again their PBE-D3 calculation is comparable with ours. The corresponding binding energy of -0.57 eV differs less than 0.02 eV from our binding energy. Moses *et al.* [65] carried out a similar analysis for benzene and naphthalene, among other molecules, and also identified the structures that we identified as the optimal adsorption sites. According to their findings, both molecules have a binding height of about 3.5 Å. No further discussion is given for the individual molecules. Their calculated distance between molecule and MoS₂ monolayer is a little bit larger than ours, which results from the use of the different functionals RPBE [68] and revPBE [69] that lead to a couple of percent too large vdW bonds [65]. Since the molecules are more separated from the monolayer, the bindings of -0.50 and -0.76 eV for benzene and naphthalene are weaker than our results suggest. In the work of Ho *et al.* [67], several configurations of anthracene on a MoS₂ monolayer have been investigated. They also found that the most strongly bound configuration is characterized by an alignment along the S-S direction. Their findings show an optimal adsorption height of 3.16 Å, which is 0.10 Å smaller than our result, and a binding energy of -1.035 eV, which varies less than 0.050 eV from the binding energy that we present.

C. Band structures

As the molecules are several angstroms away from the substrate ($\bar{h} \geq 3$ Å) and they do not form strong covalent bonds with it but are mainly bound by a weak vdW inter-

action, we can expect only slight changes on the substrate band structure due to a weak screening of the molecules. These cannot be captured in DFT but are included in the quasiparticle band structure we calculate with GdW(LDA). In addition, the molecular HOMO-LUMO gaps are much larger than the intrinsic band gap of MoS₂, thus at least one of the chemical important HOMO or LUMO states is energetically separated from the MoS₂ band gap region and can be assumed to have a negligible effect on the band gap of the corresponding adsorbate system. Indeed, this is what we can find by looking at the band structures of the adsorbate systems (one molecules that is adsorbed on a 6×6 MoS₂ monolayer supercell) that are shown in Figs. 7 and 8. In consequence of multiple umklapp processes, the direct band gap is located at the 6×6 Γ , point which includes K. The LDA band structure of these adsorbed systems is plotted in Fig. 7. We identified molecular states with a Mulliken analysis [70] and observed that the HOMO is higher in energy from benzene to naphthalene to anthracene adsorbed on the MoS₂ monolayer. To avoid any confusion, we would like to make it particularly clear that the anthracene HOMO is the highest valence band of the combined MoS₂-anthracene system and that it is doubly occupied. We have set the MoS₂ VBM to 0 eV, and thus the anthracene HOMO to the positive energy region, in order to facilitate the comparison with the two other band structures. If the LDA predictions are reasonable, benzene and naphthalene form a heterojunction of type I with the monolayer, but anthracene, whose HOMO is located between the upper most valence band and the lowest conduction band of MoS₂, would form a type II heterojunction with it. This would allow optical excitations at much lower energies because the band gap is significantly reduced from 1.637 to 1.245 eV due to the new state in the previous energy gap. Despite the decreased gap of the adsorbate system, we list the minimal direct band gap between MoS₂ states in Table IV because we are especially interested in the changes of these. However, we determined in Secs. III A 1 and III A 2 that the energy states of the molecules are much more strongly affected by the quasiparticle correction than the MoS₂ band structure, thus the HOMO is lowered so significantly in GdW(LDA) that anthracene also forms a heterojunction of type I, as we will see in the next paragraph and in Fig. 8. As mentioned, the resulting band gaps are listed in Table IV and, as we assumed, the band gap is almost not affected by the molecule in DFT. An exception is naphthalene, whose HOMO lays between the valence band splitting and hybridizes a little bit with the energetically close MoS₂ states, thus the band gap is decreased by a few meV. The other adsorbate systems are characterized by an absence of molecule states near the band edges so that no hybridization can take place there.

So far, we have just discussed the effect on the MoS₂ gap. We now want to briefly focus on the HOMO-LUMO gap of the molecules. Like we determined the HOMO in fig. 7, we are able to find the LUMO energy of the molecules in DFT. Both HOMO and LUMO are weakly hybridized with MoS₂ states, except for the anthracene HOMO. For example, in the adsorbate system of benzene, the HOMO-LUMO gap is about 5.04 eV in DFT compared to the isolated benzene value of 5.10 eV. This underlines the importance of the screening

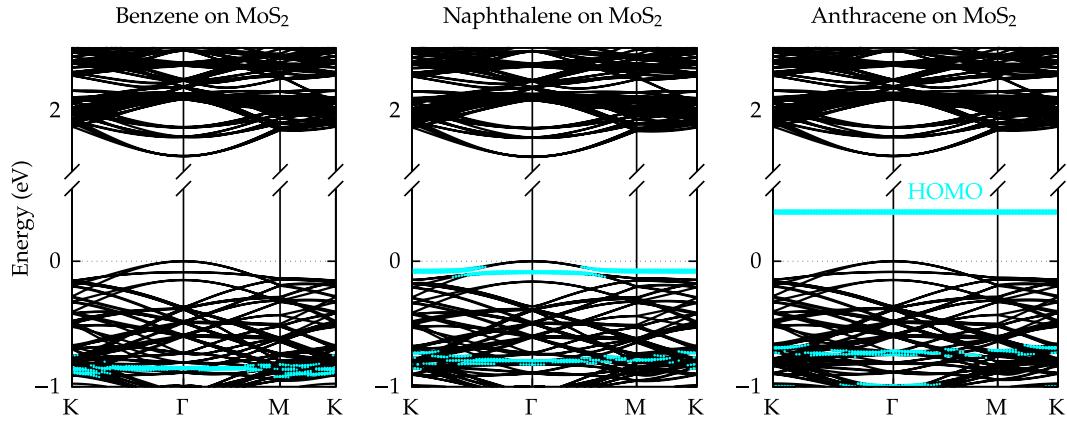


FIG. 7. LDA band structures of benzene, naphthalene, and anthracene molecules adsorbed on a MoS_2 6×6 supercell as shown in Fig. 5. Molecular energy states have been identified by a Mulliken analysis [70] and are marked by the light-blue dots. For a better comparability, the VBM of the MoS_2 monolayer is set to 0 eV and part of the band gap region is cut out. The highest plotted anthracene energy level, 0.39 eV above the MoS_2 VBM, is the occupied HOMO.

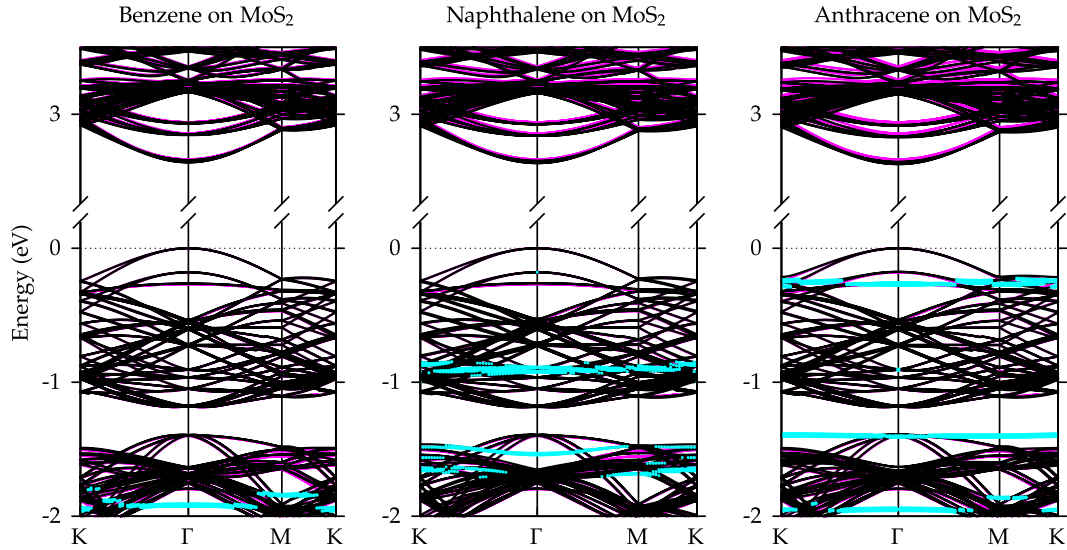


FIG. 8. Quasiparticle band structures of benzene, naphthalene, and anthracene molecule adsorbed on a MoS_2 6×6 supercell as shown in Fig. 5. In order to promote the effect the molecules have on the MoS_2 substrate, the band structure of the 6×6 supercell is shown in magenta underneath the adsorbate system band structure (black). Molecular energy states were identified by a Mulliken analysis [70] and are marked by the light-blue dots. For a better comparability, the MoS_2 VBM is set to 0 eV and part of the band gap region is cut out.

TABLE IV. Band gaps and band splittings of bare MoS_2 and MoS_2 in adsorbate systems with benzene, naphthalene, or anthracene. The DFT band gap is calculated within LDA and the quasiparticle (QP) quantities within $G\text{d}W(\text{LDA})$. $\Delta E_{\text{gap}}^{\text{QP}}$ and $\Delta(\Delta E_{\text{VB/CB}}^{\text{QP}})$ measure the difference between the band gap and the band splitting of an adsorbate system and bare MoS_2 . Gap related quantities are given in eV and band splitting related quantities are given in meV.

	$E_{\text{gap}}^{\text{LDA}}$	$E_{\text{gap}}^{\text{QP}}$	$\Delta E_{\text{gap}}^{\text{QP}}$	$\Delta E_{\text{VB}}^{\text{QP}}$	$\Delta(\Delta E_{\text{VB}}^{\text{QP}})$	$\Delta E_{\text{CB}}^{\text{QP}}$	$\Delta(\Delta E_{\text{CB}}^{\text{QP}})$
Bare MoS_2 (1×1 unit cell and 6×6 supercell)	1.637	2.648		179		16	
Benzene on MoS_2	1.637	2.641	0.007	179	0	16	0
Benzene screening + MoS_2		2.641	0.007	179	0	16	0
Naphthalene on MoS_2	1.631	2.636	0.012	179	0	16	0
Naphthalene screening + MoS_2		2.636	0.012	179	0	16	0
Anthracene on MoS_2	1.637	2.628	0.020	176	3	16	0
Anthracene screening + MoS_2		2.630	0.018	179	0	16	0

TABLE V. HOMO-LUMO gap $E_{\text{LUMO}}^{\text{HOMO}}$ of gas-phase benzene, naphthalene, and anthracene in the 6×6 supercell that we also used to calculate the quantities in Table IV, compared with the gap, which is affected by an additional screening from an MoS₂ substrate. $\Delta E_{\text{LUMO}}^{\text{HOMO}}$ measures the difference between a bare molecule and the respective molecule that is affected by the MoS₂ screening. The values are given in eV.

	$E_{\text{LUMO}}^{\text{HOMO}}$	$\Delta E_{\text{LUMO}}^{\text{HOMO}}$
Bare benzene	10.45	
Benzene + MoS ₂ screening	8.13	2.32
Bare naphthalene	8.05	
Naphthalene + MoS ₂ screening	6.00	2.05
Bare anthracene	6.47	
Anthracene + MoS ₂ screening	4.63	1.84

effects (for which a much larger difference is observed, see Table V) beyond standard DFT. Incorporating many body effects by GdW(LDA) leads to Fig. 8. First, we compare the MoS₂ substrate band structure and the adsorbate system's band structures here in order to visualize how strongly the bands are shifted or bent due to the additional molecule's electrons. We again performed a Mulliken analysis [70] and set the VBM to 0 eV. As in LDA, we can observe a higher HOMO from benzene to naphthalene to anthracene, but in this case no state crosses the valence band edge, thus all three molecules form a heterojunction of type I with the MoS₂ monolayer. And, as in LDA, the molecular states resulting from GdW are slightly hybridized with the substrate states as well, which can be seen from the slight dispersion of their bands (blue lines in Fig. 8). Furthermore, we observe small changes mainly in the conduction band region. This suggests, in combination with the fixed VBM, a rigid energy shift that increases from benzene to naphthalene to anthracene, but no significant change in the dispersion. The band gap and the band splittings are also listed in Table IV. In addition, we present the results for the primitive unit cell, the 6×6 supercell, and a model supercell including screening from the molecules but neglecting hybridization in order to easily identify the effect on the bare monolayer. For the MoS₂ model supercell with additional screening, we performed a usual GdW(LDA) calculation of this supercell but included the screening that we evaluated for the whole adsorbate system and not just the screening of the Mo and S atoms in the supercell. This is possible since we can calculate the screening of each atom in a system individually due to the model function Eq. (6). Therefore, we can take into account the screening due to the molecule without explicit treatment of its quantum mechanics and investigate the effect of this screening on the MoS₂ monolayer.

Benzene and naphthalene show similar effects on the MoS₂ substrate. The band gap is decreased by a few meV and the splittings are not affected at all. Comparing the two calculations where the adsorbed molecules are on the monolayer and the model only including the molecular screening reveals that the decrease in the band gap comes from the screening and not from any other effect. This is because there is no molecular state close to the valence or conduction band edge that might affect them. The naphthalene adsorbate system there-

fore differs fundamentally from the LDA calculation, where the HOMO slightly interacts with the VBM of the monolayer. Anthracene and the MoS₂ monolayer interact differently with each other because in this case the difference in the band gap and the valence band splitting is not identical for the adsorbate system and the monolayer with additional screening. Unlike for benzene and naphthalene, the splitting in the valence band is decreased by 3 meV compared to the bare MoS₂ and the band gap appears to be 2 meV smaller in the adsorbate system than in the substrate alone, which is influenced by the additional screening. This suggests that the anthracene HOMO, which is much closer to the MoS₂ valence band edge than it is in the case of the other two molecules, raises the VBM, thus the band gap decreases and the VBM-1 rises even more strongly (5 meV), such that the band splitting decreases more strongly than the band gap. In conclusion, the screening of anthracene is not sufficient to describe the changes in the monolayer band structure because hybridization effects play a non-negligible role in the formation of the valence band edge of this adsorbate system. Second, we investigate the effect of the MoS₂ monolayer on the HOMO-LUMO gap of the three molecules. Since these states are energetically separated by several eV, we would have to correct many bands in the supercell, which is very time consuming and demands a lot of memory. Therefore, we performed another calculation of the molecules in the same supercell without the substrate but with the screening of the whole system as an approximation of the effect of MoS₂ on the molecules. This works similarly to what we did before when we analyzed the effect of the molecule screening on the MoS₂ band gap. The HOMO-LUMO gaps of the bare molecules and with an additional screening are listed in Table V. The gaps are closing by 1.84 to 2.32 eV only due to the screening of the MoS₂ monolayer. The closing is the strongest for benzene, the weakest for anthracene and, in general, significantly stronger than the closing of the MoS₂ band gap that we discussed before. This gap was only decreased by up to 20 meV. Noori *et al.* [71] developed a screening based approximation for the HOMO-LUMO gap of small molecules, determined a screening induced benzene gap of 8.14 eV, which matches our result almost perfectly, and compared it with a GW calculated gap of 7.66 eV. Compared to their GW gap, our benzene gap is somewhat larger on an absolute energy scale, mostly due to the differences in the MBPT methods (GdW vs GW). A GW₀ calculation by Ho *et al.* [67] suggests a HOMO-LUMO gap of anthracene of 4.86 eV, which is also consistent with our findings. Approximating the HOMO-LUMO gaps by taking only the MoS₂ screening into account therefore yields good results that differ from comparable GW calculations by 5% or less. This level of accuracy is remarkable if we consider the significantly lower computational effort involved.

IV. CONCLUSION AND OUTLOOK

We started with an analysis of the bare MoS₂ monolayer and the isolated benzene, naphthalene, and anthracene molecules. Hence, we performed structural relaxations for these systems and calculated the LDA as well as the GdW(LDA) band structures and energy levels. The latter incorporates quasiparticle effects and in general leads to larger

band gaps and HOMO-LUMO gaps that are in a better agreement with experiments than the LDA results. We found that for both the MoS₂ and the molecules the quasiparticle effects are necessary to get realistic electronic structures and that the molecule states are more strongly affected by them than the MoS₂ ones, which becomes apparent by the stronger gap opening.

Based on these individual analyses, we investigated many possible geometries that benzene, naphthalene, and anthracene could take on a MoS₂ monolayer. Through careful calculations and comparisons of binding energies, we were able to identify the most stable configuration for benzene being above the sulfur atom of the MoS₂. While this molecule can center itself symmetrically above the sulfur atom because of its symmetry and size, this is not possible for naphthalene and anthracene. These molecule do not perfectly fit with the underlying monolayer in terms of size such that they align along the S-S direction. The binding energy per carbon atom decreases for the larger molecules by several percent while the distance to the MoS₂ monolayer increases by up to 0.1 Å.

Our band structure calculations that we performed for the most strongly bound adsorbate geometries with DFT and GdW(LDA) reveal that the direct band gap of a MoS₂ monolayer is not affected by the molecules in DFT. An exception is naphthalene, whose HOMO slightly hybridizes with the valence band maximum of MoS₂, which results in a little smaller gap. But there is no general mechanism that would lead to a change in the band gap. When considering quasiparticle effects within GdW(LDA), we find a decrease in the band gap that can be mainly attributed to the additional screening that comes from the adsorbed molecules. In the case of an

anthracene molecule adsorbed to the MoS₂ monolayer, the HOMO slightly hybridizes with the valence band maximum, as in the case with naphthalene in the DFT calculation, which results in a very small additional effect on the band structure that is not captured just by the screening. Anthracene is the only molecule among the investigated ones that changes the valence band splitting due to the hybridization. Lastly, we approximated how the MoS₂ substrate influences the HOMO-LUMO gap of the molecules by taking into account the screening of that substrate. We found that this screening affects the molecules two orders of magnitude more strongly than the screening of the molecules affect MoS₂.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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