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Supporting information for

Polymer interactions with Reduced Graphene Oxide: Van der Waals binding energies of Benzene on defected Graphene

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Accuracy for the S26 test set

	PBE	**vdW-DF**	**VdW-DF2**	**TS09**
Mean deviation	115	76	48	15
RMS deviation	108	60	42	16

Tab.S1: Noncovalent binding energy differences to the CCSD results for S26 set of molecular pairs in meV.

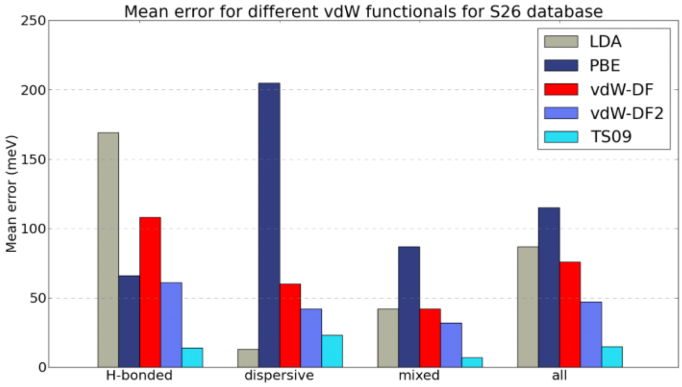


Fig. S1: Mean vdW energy errors belonging to different categories of molecules in S26 database.

We evaluate our implementation of the TS09 functional in the GPAW code versus other commonly used functionals by measuring the dispersion interaction within the S26 database dimers. The S26 is the S22[i] set of non-covalently bound molecules extended by 4 single hydrogen bonded complexes[ii]. In Table S1, the energy mean- and RMS- deviations compared to the accurate coupled cluster calculations are listed and graphically compared in fig. S1. Both TS09 and vdW-DF give substantially increased accuracy for week non-covalent interactions as compared to LDA or PBE.

Control study

Our 591 meV benzene-graphene binding energy using the TS09 functional is in good agreement the literature value of 575 meV[iii]. In addition, we obtain the inter-sheet binding energy per atom in graphite of 85 meV at the equilibrium separation of 3.3 Å for TS09 and 43 meV at the equilibrium separation of 3.6 Å for vdW-DF in agreement with other calculations[iii,iv]. The overestimation of the BE by the TS09 functional for extended systems in comparison with the experimental value (52±5 meV per atom in graphite[v]) is known[iv] and is contrasted here by the better performance of TS09 for dispersion interactions of the small molecule S26 test set[iv]. Our vdW-DF binding energy of 429 meV between benzene and graphene is 10~20% lower than the values reported in literature (481 meV, 495 meV)[iii,vi]. A reason for this deviation might be that in the GPAW implementation only the PAW smooth valence electron density is used for the evaluation of the non-local exchange energy [c.f. eq.

(2) in the main text). However, we note, that the energies are consistent with the statement, that only 91% of the full interaction can be gained in a cell similar to ours in these references. We cannot reproduce the remaining 10% energy contribution by increasing the cell size. A cell, nine times larger than the one used in this work (i.e. 540 atoms in the graphene sheet), has not considerably enhanced the binding energy. We found the energy to be converged inside 5meV already with the standard cell defined above. Allowing for structural relaxations of the benzene-graphene compound system leads to bending of the substrate under the benzene molecule and improved binding (470 meV). In any case, these small deviations do not affect the conclusions drawn.

Structures of defected graphene

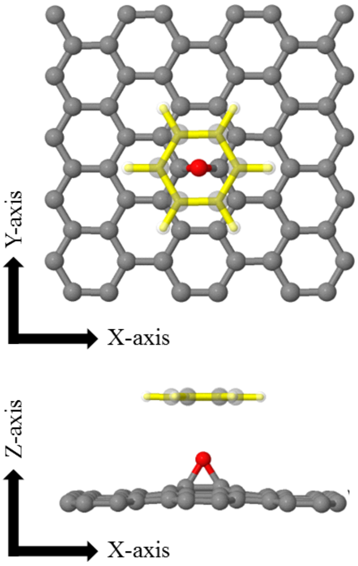
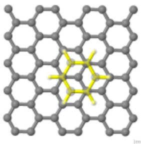
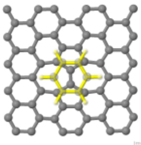
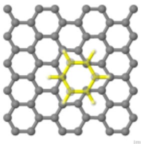
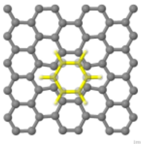
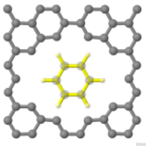
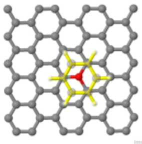
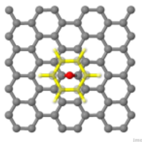
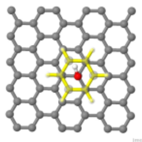
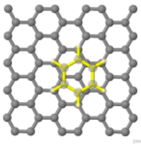
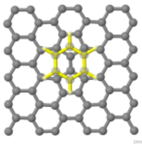
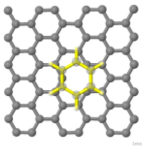
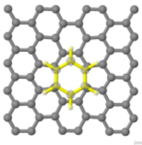
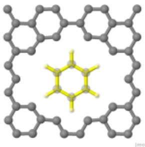
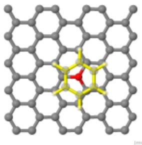
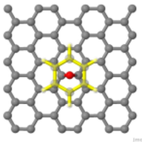
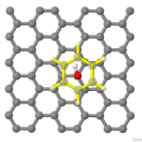
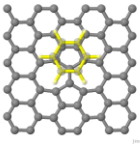
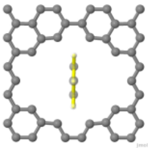
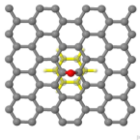
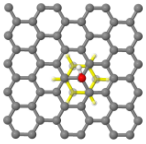
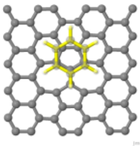
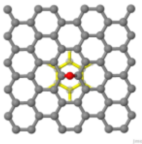
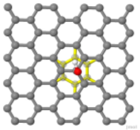
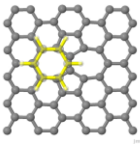
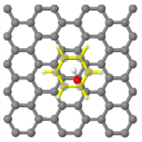
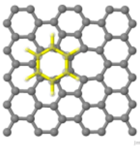


Fig. S2: The supercell considered in this work with a sample defect. Here, Benzene is adsorbed on top on an oxygen adsorbent (epoxy group) on the surface of graphene sheet.

A pristine	B 55-77	C SV	D DV	E Hole	F Ox-doped	G Ox-epoxy	H OH
 **1**							
 **2**							
3							
4							
5							
6							

Tab. S2: Overview of the defects investigated in this work.

A: pristine graphene (1: AB, 2: rotated)

B: 55-77 (1: border-AB, 2: border-rotated, 3: 5ring-AB , 4:5ring-rot., 5: 7ring-AB, 6:7ring-rot.)

C: single vacancy (1: AB, 2: rotated)

D: double-vacancy (1: AB, 2: rotated)

E: big hole (1: AB, 2:rotated, 3: through perp-AB)

F: Oxygen-filled vacancy (1: AB, 2: rotated)

G: epoxy (1: AB, 2:rotated, 3: below AB, 4:rotated)

H: OH (1: on O atom-AB , 2: on O atom-rotated, 3: below AB, 4: below rotated, 5: on H atom-AB)

Defect Configurations

Here we discuss the considered defects in detail.

B: 55-77

The typical Stone-Walls defect is formed by rotating two bonded carbon atoms 90° in the plane. After optimization without benzene, two five and two seven rings were formed, with symmetric configurations. The CC bond shared between the two seven-membered rings has a length of 1.301 Å while the other bonds in the 7 rings are 1.457 Å (two bonds) and 1.46 Å (two bonds) and 1.441 Å (two bonds). In the 5 rings, bonds were 1.457 Å (two bonds) and 1.373 Å (two bonds) and 1.42 Å (one bond.)

When the symmetry is broken by the desorbed benzene molecule and relaxation is considered, the defect bulges out of the plane. The resulting corrugated structure has an effective thickness of 1.21 Å as shown in Fig.2. in the main text.

C: single vacancy

The single vacancy defect is subject to the following geometrical changes after the structural optimization without benzene: the three nearest neighbors recede away from the vacancy. Their contact angles with carbons in the rest of the crystal increase to be 122.4°,122.4°,126° instead of the 120° typical of the honeycomb network. The two atoms with identical contact angles lie in the zigzag axis pointing away from the vacancy and also contract bonds with their remaining neighbors to 1.403 Å and 1.385 Å . The third neighbor contracts its bonds symmetrically to be 1.377 Å for both neighbors, and its position relative the vacancy defines an armchair axis of the crystal.

Symmetry breaking on the SV defect produces a slight bend in the surrounding area. One of the three carbons with dangling bonds sticks 0.6 Å below the graphitic plane, while the rest bend in the scheme shown in Fig.2. in the main text.

D: double vacancy

As for the double vacancy defect, the removal of two carbons leads to a *quasi*-585 topological defect and defines symmetry axes relative to which identical changes are witnessed. Each one of the four nearest neighbors to the missing two carbons contact the lattice at reduced angles (113.3° each). Bond lengths in the two five-membered rings are 1.4 Å (two bonds), 1.403 Å (two bonds), 1.934 Å (shared with the eight-membered) and in the eight-membered are 1.451 Å (four bonds), 1.456Å (two bonds), 1.934 Å (two shared with the five-membered).

F: oxygen-filled vacancy

In oxygen-doped graphene, the impurity atom lies in the plane with a slight bump of 0.24 Å. The surrounding C-O bond lengths are 1.494 Å (two bonds) and 1.498 Å (one bond).

G: epoxy

A single oxygen atom sits preferably on top of graphene connecting two carbon atoms in the bridge position and forms an epoxy defect[vii]. The C-O-C triangle formed has the bond lengths is (1.46 Å, 1.46 Å, 1.514 Å) and angles (58.8°, 58.8°, 62.4°). The triangle base is lifted by 0.63 Å above the level of the graphene sheet (far away from the defect), and is connected to the rest of substrate via four closest neighbors with 1.465 Å bond length each. A slight overall concave curvature is resulting in the simulation cell.

H: OH

The hydroxyl (OH) group chemically adsorbs on graphene and relaxes to position where the oxygen atom is placed almost exactly on top of one carbon atom (shifted at most with 0.1 Å in the plane projection). The base carbon atom is lifted to 0.67 Å above the plane with a C-O bond length of 1.506 Å. The O-H bond length is 0.981 Å and the triangle H-O-C open an angle of 106°. The star-like bonds branching from the base carbon experience stretching and their lengths become 1.497 Å each. We obtain a binding energy of OH on the graphene sheet of 0.71 eV in excellent agreement in particular with other PAW approaches.

Van der Waals detailed energetics

The pristine graphene surface and many of the defects are spin-saturated and contain no radicals. Therefore these calculations have been performed without consideration of spin degrees of freedom. However, some of the considered defects contain additive oxygen atoms or radical groups, where we allowed relaxation of the spin also. Enforcing spin-polarized calculation had a very weak influence on the van der Waals interaction energy.

Structures	**vdW-DF**		**TS09**	
	BE (meV)	**AH (Å)**	**BE (meV)**	**AH (Å)**
A1	429	3.58	591	3.33
A2	427	3.59	582	3.34
B1	359	2.98	570	2.75
B2	339	2.91	587	2.76

B3	494	2.91	689	2.75
B4	519	2.93	691	2.74
B5	314	3.05	564	2.86
B6	350	3.03	557	2.85
C1	398	3.3	409	3.12
C2	387	3.23	513	3.11
D1	381	3.64	481	3.39
D2	378	3.64	479	3.39
E1	372	2.41	551	1.81
E2	365	2.42	520	2.01
E3	281	3.3	341	2.7
F1	474	3.55	635	3.33
F2	473	3.56	624	3.34
G1	167	4.93	183	4.87
G2	162	4.92	184	4.9
G3	463	3.25	642	2.97
G4	456	3.26	634	2.99
H1	149	5.43	183	5.31
H2	147	5.43	182	5.32
H3	439	3.34	611	3.07
H4	440	3.35	600	3.09
H5	163	5.39	207	5.25

Tab.S3:The binding energies (BE) and absorption heights (AH) of all defects studied in this work.

Geometrical effect of the van der Waals interaction

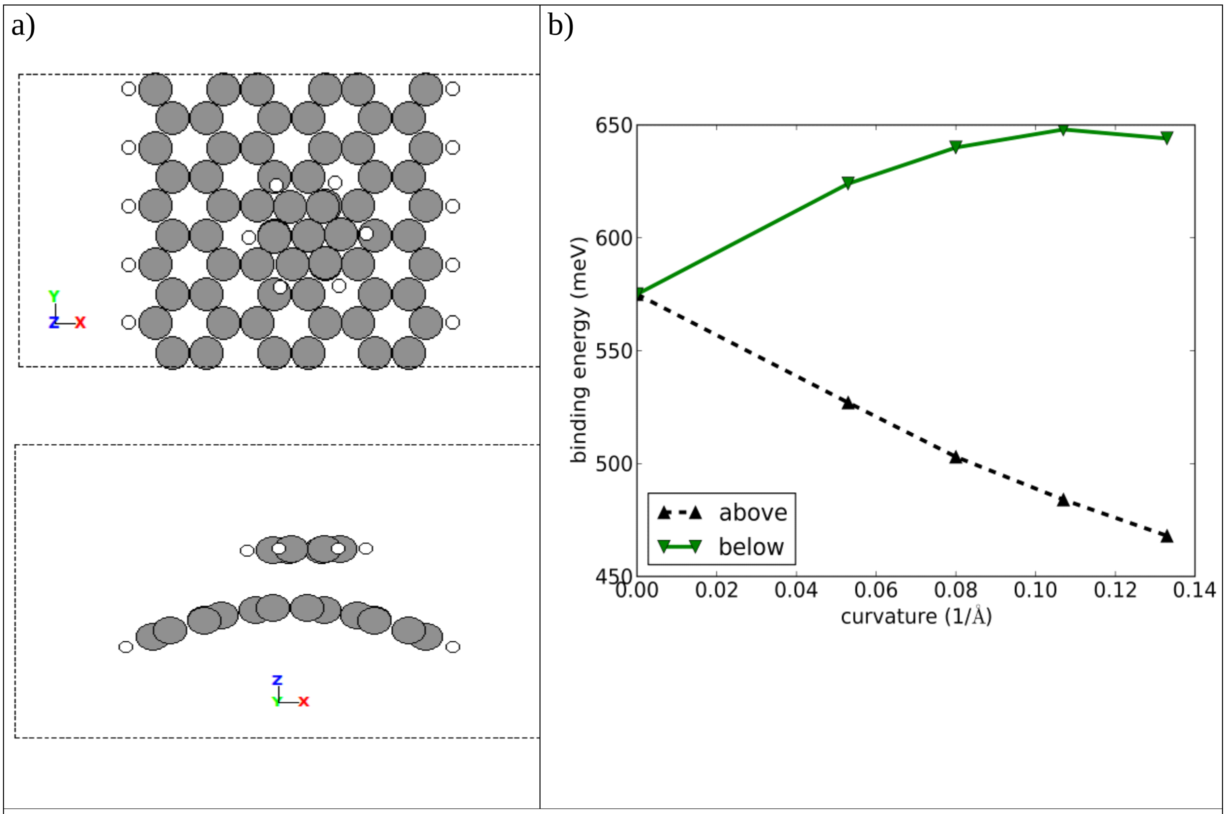


Fig. S3: a) Top and side view of the configurations used to explore the geometric effect in van der Waals interactions between benzene and graphene. The unit cell borders and coordinate directions are indicated. The configuration depicted corresponds to a curvature of 0.107 $Å^{-1}$. b) Binding energies depending on curvature.

We have also investigated how the degree of curvature influences the adsorption of a benzene molecule to either side of the substrate. We have used a graphene ribbon (60 carbon atoms, CC bond length = 1.42 Å) for this purpose, where the two zigzag edges are passivated with hydrogens (with CH bond length equals 1.12 Å). Periodic boundary conditions (BC) are applied to the *y*-direction and zero BC in the other directions (see fig. S3). In order to create a defined curvature, the atoms in the ribbon are displaced vertically according to their *x*-position, such that their *z*-coordinate is given by

$$z = A\cos((x - x_{CM})\pi\ /L) \tag{1}$$

where x_{CM} is the *x*-position of the ribbons' center of mass and L=13.6 Å. This corresponds to an effective curvature (inverse radius R) of $\frac{1}{R} = A\left(\frac{\pi}{L}\right)^2$. Similar to configuration A1, the benzene molecule is placed on-top in AB configuration and no further structural optimization is considered. The TS09 binding energy is calculated by uniformly displacing benzene vertically above and below the ribbon to scan the energy landscape. Fig S3 b) shows that the binding energy diminishes above and increases below the graphite plane with increasing curvature. The effect is approximately linear in for small curvatures. It saturates for benzene below the surface due to the constraints in the concave configuration.

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