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Adsorption of H₂O, NH₃, CO, NO₂, and NO on graphene: A first-principles studyO. Leenaerts,^{*} B. Partoens,[†] and F. M. Peeters[‡]*Departement Fysica, Universiteit Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium*

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Motivated by the recent realization of graphene sensors to detect individual gas molecules, we investigate the adsorption of H₂O, NH₃, CO, NO₂, and NO on a graphene substrate using first-principles calculations. The optimal adsorption position and orientation of these molecules on the graphene surface is determined and the adsorption energies are calculated. Molecular doping, i.e., charge transfer between the molecules and the graphene surface, is discussed in light of the density of states and the molecular orbitals of the adsorbates. The efficiency of doping of the different molecules is determined and the influence of their magnetic moment is discussed.

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I. INTRODUCTION

The synthesis of monolayer graphite (i.e., graphene)¹ and the experimental observation of Dirac charge carriers in this system^{2,3} have awakened an enormous interest in this two-dimensional material. The unusual properties of carriers in graphene are a consequence of the gapless and approximately linear electron dispersion at the vicinity of the Fermi level at two inequivalent points of the Brillouin zone. In the low-energy limit, the quasiparticles in these systems are described in terms of massless chiral relativistic fermions governed by the Dirac equation.

The good sensor properties of carbon nanotubes are already known for some time,⁴ but recently, the possibility to use graphene as a highly sensitive gas sensor was also reported.⁵ It was shown that the increase in graphene charge carrier concentration induced by adsorbed gas molecules can be used to make highly sensitive sensors, even with the possibility of detecting individual molecules. The sensor property is based on changes in the resistivity due to molecules adsorbed on the graphene sheet that act as donors or acceptors. The sensitivity of NH₃, CO, and H₂O up to 1 ppb (parts per 10⁹) was demonstrated, and even the ultimate sensitivity of an individual molecule was suggested for NO₂. These excellent sensor properties of graphene are due to two important facts: (i) graphene is a two-dimensional crystal with only a surface and no volume, which maximizes the effect of surface dopants, and (ii) graphene is highly conductive and shows metallic conductance even in the limit of zero carrier density.

To fully exploit the possibilities of graphene sensors, it is important to understand the interaction between the graphene surface and the adsorbate molecules. We perform in this letter first-principles calculations for the molecules NH₃, NO₂, NO, CO, and H₂O adsorbed on graphene. We determine their exact orientation on the surface and their preferential binding site by calculating their binding energy. Their charge transfer to the graphene surface is investigated in order to determine the donor or acceptor character of the molecular dopant.

II. COMPUTATIONAL DETAILS

The first-principles calculations are performed using density functional theory (DFT) which has been successfully

used for the study of molecular adsorbates on single-walled (carbon) nanotubes (SWNT).^{6–10} All our DFT calculations were carried out with the ABINIT code,¹¹ within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof.¹² The advantage of GGA over the local density approximation (LDA) in this work is that the GGA will not lead to a strong bonding of the molecules as in LDA. So, if the molecules bind in GGA, they will definitely bind in a real system (and in LDA) too. The distance between adsorbate and the graphene surface, however, will be somewhat overestimated and consequently the binding energy will be underestimated.

We use a plane wave basis set with a cutoff energy of 816 eV and pseudopotentials of the Troullier–Martins type.¹⁴ For the adsorption of the molecules NH₃, CO, and H₂O, we use non-spin-polarized calculations, while for NO₂ and NO, we use spin-polarized ones. The total system consists of a 4 × 4 graphene supercell (32 C atoms) with a single molecule adsorbed to it (Fig. 1) and with a distance of 16 Å between adjacent graphene layers. The sampling of the Brillouin zone is done using a 5 × 5 × 1 Monkhorst–Pack¹⁵ grid, which is tested to give converged results for all the properties we calculate. For the calculation of the density of states (DOS), we use a 15 × 15 × 1 Monkhorst–Pack grid and a Gaussian smearing of 0.14 eV.

Charge transfers are calculated based on the Hirshfeld charge analysis.¹⁶ The atomic charge Q_A for each atom is obtained by [with $\rho(\mathbf{r})$ the calculated density and $\rho_A^0(\mathbf{r})$ the electron density computed for the isolated atom A and taken from Ref. 11]

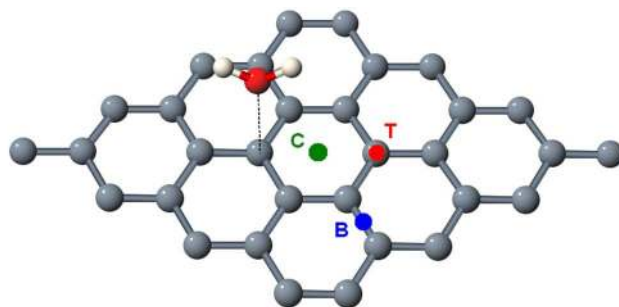


FIG. 1. (Color online) H₂O on graphene. 4 × 4 supercell of graphene with adsorbed H₂O molecule.

$$Q_A = \int \frac{\rho_A^0(\mathbf{r})}{\sum_{A'} \rho_{A'}^0(\mathbf{r})} \rho(\mathbf{r}) d\mathbf{r},$$

from which the charge transfer (ΔQ) is deduced. From this result we determined whether or not the adsorbate acts as an acceptor or a donor. It should be noted that the size of the charge transfer is slightly dependent on the method used to calculate it.

The distance from the adsorbate to the graphene surface is calculated from the difference in weighted averages of the different atoms of the molecule and the carbon atoms of the graphene sheet, where we used the atomic number Z of the atoms as the weight factor.

III. RESULTS

For each adsorbate, three adsorption sites are considered, namely, on top of a carbon atom (T), the center of a carbon hexagon (C), and the center of a carbon-carbon bond (B) (see Fig. 1). For these positions, different orientations of the molecules are examined and the adsorption energy is calculated for all of them. The adsorption energy (E_a) is the energy of the isolated graphene sheet and isolated molecule minus the energy of the fully relaxed graphene sheet with the molecule adsorbed to it. We did not correct these energies for the dipole-dipole interactions which occur due to the finite size of the supercells. However, these energies mainly cancel, resulting in corrections of the order of 2 meV in the worst cases (H_2O and NH_3). This has no influence on any of our conclusions, so we decided to neglect them. The strength of the molecular doping is discussed in light of the density of states and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the adsorbate. The position of these orbitals, visible as peaks in the DOS, is practically independent of the orientation and adsorption site of the molecule, so we only show the total DOS for one geometry per molecule. We can now distinguish two charge transfer mechanisms: (i) a charge transfer can occur due to the relative position in the DOS of the HOMO and LUMO of the adsorbate. If the HOMO is above the Fermi level of pure graphene (the Dirac point), there is a charge transfer to graphene. If the LUMO is below the Dirac point, charge will transfer to the molecule. (ii) The charge transfer between adsorbate and graphene is also partially determined by the mixing of the HOMO and LUMO with the graphene orbitals (hybridization). This mixing scales with the overlap of the interacting orbitals and the inverse of their energy difference.

It is more difficult to discuss the adsorption energy in this way because of the large amount of possible interacting orbitals present in graphene. Our investigation starts with the nonmagnetic molecules H_2O , NH_3 , and CO , followed by the paramagnetic ones, NO_2 and NO . We discuss the molecules in the order of increasing complexity of their charge transfer mechanism.

A. H_2O on graphene

We examine the following orientations of the H_2O molecule with respect to the graphene surface: starting from the

TABLE I. H_2O on graphene: the adsorption energy (E_a), the distance of H_2O above the graphene surface (d), and the charge transfer from the molecule to graphene (ΔQ) for ten different geometries.

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
B	u	18	3.70	0.021
T	u	19	3.70	0.021
C	u	20	3.69	0.021
B	n	24	3.55	0.013
T	n	24	3.56	0.015
C	n	27	3.55	0.014
B	d	18	4.05	-0.009
T	d	19	4.05	-0.009
C	d	19	4.02	-0.010
C	v	47	3.50	-0.025

O atom the H-O bonds pointing up (u), down (d), or parallel to the graphene surface (n). Another orientation (v) was suggested in a theoretical study, based on an empirical method, of the adsorption of H_2O on graphite.¹³ This orientation has one O-H bond parallel to the surface and the other one pointing to the surface. All properties were found to be almost invariant with respect to rotations around the axis perpendicular to the surface and through the oxygen atom, and therefore, we will not discuss this orientation. The results of the calculations are given in Table I.

From Table I, we learn that all the adsorption energies are small, which is partially a consequence of the calculation method. This is not very important because the adsorption energies are only used to compare the different geometries and to find the best position and orientation of the molecule for which we need only relative values. Table I also shows that the adsorption energy is primarily determined by the orientation (u, d, n, and v) and to a lesser degree by the position (C, B, and T) of the molecule. The energy differences are 5–6 meV with respect to the orientation, but they vary with about 1–2 meV when changing the position. This difference in importance of position and orientation is even more pronounced when we look at the charge transfers. If the O atom points to the graphene surface, there is a (small) charge transfer to graphene, but if the H atoms point to the surface, there is a small charge transfer to the water molecule. This is a consequence of the form of the HOMO and LUMO of H_2O and their relative position with respect to the Dirac point (see Fig. 2).

The HOMO ($1b_1$) is completely located on the O atom, but the LUMO ($4a_1$) is mostly located on the H atoms. In the u orientation, the HOMO plays the dominant role and donates, through a small mixing with graphene orbitals above the Fermi level, some charge to graphene. There is also a (stronger) mixing with the orbitals below the Dirac point because they are closer in energy, but this does not induce any charge transfer because all these orbitals are filled. In the d and v orientations, the LUMO of H_2O interacts stronger with the surface and is able, through a small mixing with the

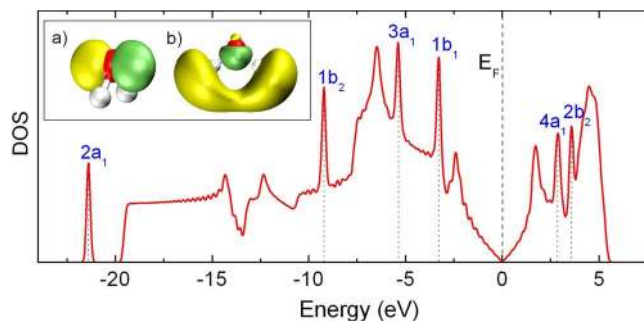


FIG. 2. (Color online) H₂O on graphene. Inset: (a) the HOMO and (b) the LUMO of H₂O (the H atoms are white and the oxygen atom is red; green and yellow indicate different signs of the orbital wave function). Main panel: DOS of H₂O on graphene. The blue dotted lines show the positions of the molecular orbitals of H₂O.

graphene orbitals below the Dirac point, to accept some charge from graphene. There is also a stronger mixing with orbitals above the Dirac point now, but this does not induce any charge transfer because all these orbitals are empty. In the *n* orientation, it is again the HOMO that will interact stronger, but now there is also some interaction with the LUMO. There will be a charge transfer from the molecule to graphene, but because of the interaction with the LUMO, it will be smaller.

Experimentally,⁵ one finds that H₂O acts as an acceptor on graphene which is in accordance with our theoretical results where we find that the acceptor character (*C*, *v*) is energetically favored on perfect graphene.

B. NH₃ on graphene

Two orientations of the ammonia molecule were investigated, one with the H atoms pointing away from the surface (*u*) and the other with the H atoms pointing to the surface (*d*). All properties were again found to be almost invariant to rotations around the axis perpendicular to the surface and through the nitrogen atom. The results of the calculations are given in Table II. The adsorption site and the orientation are now seen to be of the same importance for the adsorption energy. The charge transfer, however, is solely determined by the orientation of the NH₃ molecule.

TABLE II. NH₃ on graphene: the adsorption energy (E_a), the distance of NH₃ above the graphene surface (d), and the charge transfer from the molecule to graphene (ΔQ) for six different geometries.

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
B	<i>u</i>	21	3.86	0.026
T	<i>u</i>	20	3.86	0.026
C	<i>u</i>	31	3.81	0.027
B	<i>d</i>	15	4.08	0.001
T	<i>d</i>	16	3.97	0.000
C	<i>d</i>	25	3.92	-0.001

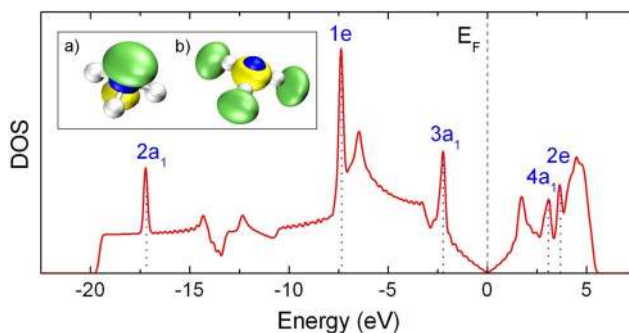


FIG. 3. (Color online) NH₃ on graphene. Inset: (a) the HOMO and (b) the LUMO of NH₃ (the N atom is blue and the H atoms are white). Main panel: DOS of NH₃ on graphene.

There is a small charge transfer from the molecule to the graphene surface of $0.03e$ in the *u* orientation and there is (almost) no charge transfer in the *d* orientation. We can see how this comes about by looking at the HOMO ($3a_1$) and LUMO ($4a_1$) of the NH₃ molecule [Figs. 3(a) and 3(b)]. In the *u* orientation, the HOMO is the only orbital that can have a significant overlap with the graphene orbitals and thus can cause charge transfer. As a consequence, the NH₃ molecule will act as a donor. In the *d* orientation, both HOMO and LUMO can cause charge transfers which are similar in magnitude but in opposite directions. The net charge transfer is therefore close to 0. The *u* orientation is energetically favored which explains the donor character as observed experimentally.⁵

We also performed LDA calculations for the adsorption of NH₃ on graphene. The results of these are similar for the charge transfer, but the adsorption energy is much larger (± 100 meV). The real adsorption energy is known to lie between the two approximate values obtained through GGA and LDA. This is consistent with the experimental observation⁵ that the adsorbates can be removed from the surface by annealing at 150 °C.

C. CO on graphene

Three different orientations were used for the CO molecule. Two with the molecule perpendicular to the surface, with the O atom above the C atom (*u*) and the other way around (*d*), and one parallel to the surface (*n*).

From Table III, we notice that the CO molecule always acts as a donor. The size of the charge transfer only depends on the orientation of the molecule with respect to the surface (Fig. 4). The differences in charge transfer are due to differences in orbital overlap between the HOMO (5σ) of the CO molecule and graphene. The LUMO (2π) seems to play no important role in the doping process although it is closer to the Dirac point than the HOMO. To understand this, we have to take into account the symmetry of this orbital and the graphene orbitals. The DOS below and close (< 3 eV) to the Dirac point originates from (mostly) bonding combinations of the p_z atomic orbitals of the C atoms of graphene. The DOS above the Dirac point is mostly due to antibonding combinations. The completely antisymmetric LUMO will

TABLE III. CO on graphene: the adsorption energy (E_a), the distance of CO above the graphene surface (d), and the charge transfer from the molecule to graphene (ΔQ) for seven different geometries.

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
B	u	10	3.75	0.019
T	u	10	3.75	0.019
C	u	13	3.73	0.019
T	d	8	3.72	0.009
C	d	10	3.70	0.010
B	n	14	3.74	0.013
C	n	14	3.74	0.012

therefore mostly interact with the DOS above the Dirac point which does not cause any doping.

The HOMO is thus the more important orbital and the charge transfer is consequently always to graphene. Because the HOMO is mainly located on the C atom, the charge transfer is largest when the C atom is closest to the surface (u orientation), smallest when the O atom is closer to the surface (d orientation), and intermediate when both atoms are at an (almost) equal distance from the surface (n orientation).

D. NO₂ on graphene

In Ref. 17, it was stated that adsorbates with a magnetic moment in general result in a larger doping. Therefore, we will now turn our attention to paramagnetic molecules. The first one is NO₂ which has, in a spin-polarized calculation, an energy that is 0.4 eV smaller as compared to an unpolarized one and therefore is paramagnetic. We examine three different orientations of the NO₂ molecule: starting from the N atom, the N-O bonds pointing up (u), down (d), or parallel to the graphene surface (n).

The LUMO ($6a_1, \downarrow$) of NO₂ is located 0.3 eV below the Dirac point (Fig. 5). This induces a large charge transfer to the molecule. However, there are also some NO₂ orbitals close enough to the Dirac point to cause some charge transfer in the opposite direction through orbital mixing [especially the HOMO ($6a_1, \uparrow$)] [Table IV]. The latter charge transfer is

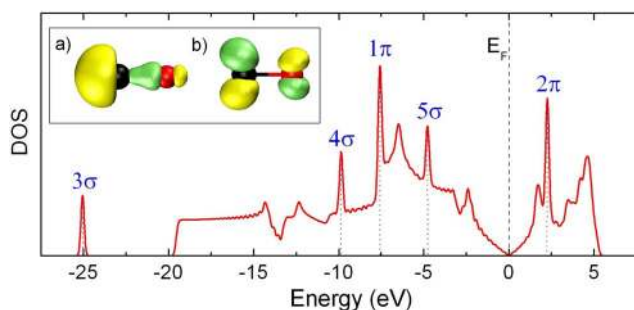


FIG. 4. (Color online) CO on graphene. Inset: (a) the HOMO and (b) the LUMO of CO (the C atom is black and the O atom is red). Main panel: DOS of CO on graphene.

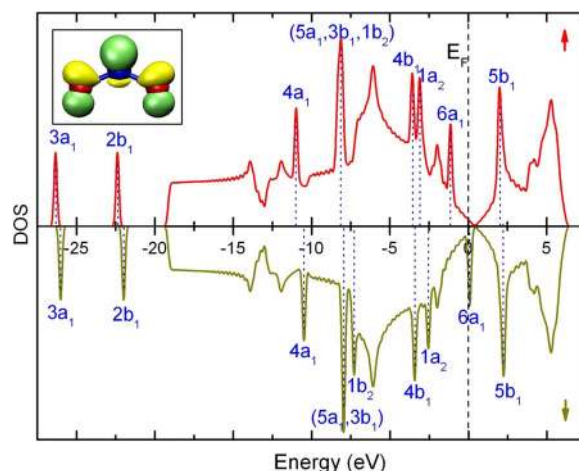


FIG. 5. (Color online) NO₂ on graphene. Inset: HOMO and LUMO of NO₂ (the N atom is blue and the O atom is red). Main panel: spin-polarized DOS of NO₂ on graphene.

smaller than the first one but it is still noticeable in the strength of the magnetic moment of the system. The total magnetic moment of graphene and adsorbate in, e.g., the (B, d) orientation is $0.862\mu_B$. The charge transfer from graphene ($M=0\mu_B$) to NO₂ ($M=1\mu_B$) is $0.099e$, so the orbital mixing causes a charge transfer of $\pm 0.039e$ to graphene.

E. NO on graphene

To test whether or not there is always strong doping by paramagnetic molecules, we will investigate another one. For NO, a spin-polarized calculation gives an energy that is 0.3 eV lower than a non-spin-polarized one, so NO is indeed a paramagnetic molecule. We investigate the same orientations and use the same notations as for the CO molecule (replace C with N). Contrary to the claim made in Ref. 17, we did not find that NO induces any strong doping. The charge transfers are an order of magnitude smaller than in the case of the NO₂ molecule (see Table V) which is comparable to the nonmagnetic molecules. Physically, we can understand this if we compare the DOS of the adsorbates NO (Fig. 6) and NO₂ on graphene. For NO₂ adsorbed on graphene, the LUMO is situated 0.3 eV below the Dirac point of graphene.

TABLE IV. NO₂ on graphene: the adsorption energy (E_a), the distance of NO₂ above the graphene surface (d), and the charge transfer from the molecule to graphene (ΔQ) for six different geometries.

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
B	d	67	3.61	-0.099
T	d	65	3.61	-0.099
C	d	63	3.64	-0.098
B	u	55	3.83	-0.089
T	u	55	3.93	-0.090
C	n	67	3.83	-0.102

TABLE V. NO on graphene: the adsorption energy (E_a), the distance of NO above the graphene surface (d), and the charge transfer from the molecule to graphene (ΔQ) for six different geometries.

Position	Orientation	E_a (meV)	d (Å)	ΔQ (e)
C	u	16	4.35	0.006
T	u	14	4.35	0.006
C	d	13	4.11	0.007
T	d	11	4.27	0.005
C	n	28	3.71	0.018
B	n	29	3.76	0.017

This induces a strong doping. In the case of NO (Fig. 6), the HOMO is degenerate ($2\pi_x, 2\pi_y$) and is half filled (so it is also the LUMO) and lies only 0.1 eV below the Dirac point. This induces a very small charge transfer from graphene to NO, but due to its small strength, it can be (over)compensated by orbital mixing. The HOMO and/or LUMO, of NO can, because it is half filled, cause charge transfer in both directions by mixing with the graphene orbitals below and above the Dirac point. However, as in the case of the LUMO of CO, it interacts mostly with the latter due to symmetry reasons. So, the orbital mixing leads to charge transfer to graphene.

We see from Table V that the charge transfer due to orbital mixing always overcompensates the small transfer due to the position of the HOMO and/or LUMO, so NO always act as a donor. We notice that there are large differences in ΔQ and in the distance d . They are obviously correlated because a smaller distance between adsorbate and graphene leads to a larger orbital overlap and consequently to more orbital mixing (i.e., a larger charge transfer). The differences in the distance can be explained by the overlap of the 5σ orbital. The position of this orbital is very close in energy to that part of the graphene DOS that originates from the (bond-

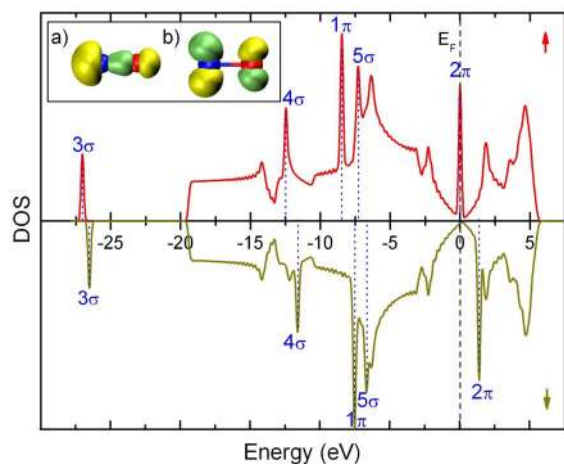


FIG. 6. (Color online) NO on graphene. Inset: (a) 5σ orbital and (b) HOMO/LUMO of NO (the N atom is blue and the O atom is red). Main panel: spin-polarized DOS of NO on graphene.

TABLE VI. Summary of results.

Adsorbate	Theory	Expt. ^a	E_a (meV)	ΔQ (e)
H ₂ O	Acceptor	Acceptor	47	-0.025
NH ₃	Donor	Donor	31	0.027
CO	Donor	Donor	14	0.012
NO ₂	Acceptor	Acceptor	67	-0.099
NO	Donor		29	0.018

^aReference 5.

ing) combinations of carbon p_z orbitals around the Γ point. Mixing of these orbitals induces a net energy shift upward so they repel each other strongly. The geometry of the 5σ orbital gives a large overlap in the u orientation, a smaller overlap in the d orientation, and the smallest overlap in the n orientation. This gives a simple explanation for all the differences found from our calculations.

IV. SUMMARY AND CONCLUSIONS

The charge transfer between the considered adsorbates and graphene is found to be almost independent on the adsorption site but it does depend strongly on the orientation of the adsorbate with respect to the graphene surface. We compared two paramagnetic molecules, NO₂ and NO, and found that NO₂ induces a relatively strong doping ($-0.1e$), but NO does not ($<0.02e$). This is in contrast to Ref. 17 where it was claimed that paramagnetic molecules are strong dopants which we found indeed to be the case for NO₂ but not so for NO.

For the considered adsorbates, the sign of the charge transfer agrees with what was found experimentally (see Table VI) in Ref. 5. We showed that these charge transfers can be understood from two charge transfer mechanisms. In NO₂ on graphene, it is mainly due to the position of the LUMO below the Dirac point for all the other studied adsorbates it is caused by the mixing of the HOMO or LUMO orbitals with the orbitals of graphene. The strength of this hybridization can be deduced from the geometrical orientation of the HOMO and LUMO orbitals with respect to the graphene surface.

The strength of the charge transfer and the binding energies must be seen in light of the used approximations (GGA) and the method of calculation (Hirshfeld method), which probably lead to an underestimation. The trends and relative values, on the other hand, are much more trustworthy.

Our results are also in good agreement with theoretical studies of the adsorption of molecules on large SWNTs in, e.g., Ref. 6. This suggests that some of the knowledge of adsorption on nanotubes should be transferable to graphene.

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