

Supporting Information for: "Chemisorption of Hydroxide on 2D Materials From DFT Calculations: Graphene Versus Hexagonal Boron Nitride"

Benoit Grosjean,[†] Clarisse Péan,[†] Alessandro Siria,[‡] Lydéric Bocquet,[‡] Rodolphe
Vuilleumier,[†] and Marie-Laure Bocquet^{*†}

*École Normale Supérieure-PSL Research University, Département de Chimie, Sorbonne
Universités - UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24, rue Lhomond,
75005 Paris, France, and École Normale Supérieure-PSL Research University, Laboratoire
de Physique Statistique, UMR 8550, 24, rue Lhomond, 75005 Paris, France*

*To whom correspondence should be addressed

[†]École Normale Supérieure-PSL Research University, Département de Chimie, Sorbonne Universités - UPMC Univ Paris 06, CNRS UMR 8640 PASTEUR, 24, rue Lhomond, 75005 Paris, France

[‡]École Normale Supérieure-PSL Research University, Laboratoire de Physique Statistique, UMR 8550, 24, rue Lhomond, 75005 Paris, France

Neutral system with K counterion

The adsorption energies of hydroxyde on BN and graphene layers in a neutral supercell containing a potassium cation as counterion were found remarkably close to the energies obtained without including the counterion (see Table 1). Since the presence of a counterion far from the hydroxyde and the surface is only relevant if a solvent is present, one should especially compare adsorption energies obtained within the implicit water approach. In water, the differences in adsorption energies between the systems with and without the potassium cation were found to be less than 70 meV.

Table 1: Adsorption energy of a hydroxyde on BN and graphene layers in vacuum and in implicit water with and without a potassium counterion present in the supercell. The distance between the counterion and the oxygen atom of the hydroxyde as well as the distance of the potassium to the surface are also displayed. Only electronic optimizations were performed for the case including the counterion.

	With Potassium		Without Potassium	
	BN Layer	Graphene Layer	BN Layer	Graphene Layer
E_{ads} in Vacuum (eV)	-1.44	-.44	-2.3	-.5
E_{ads} in Implicit Water (eV)	-.83	+.38	-.89	+.33
K - O Distance (Å)	7.71	7.71	-	-
K - Surface Distance (Å)	4.84	4.78	-	-

Atomic charges

Table 2: Mulliken atomic charges expressed in elemental charge. $\langle Q_i \rangle$ is the average atomic charge of atoms i and Q_i^* is the atomic charge of the adsorption site. Values are presented for adsorbed and desorbed states of a hydroxyle and a hydroxyde on both materials, as well as charges of the pristine surfaces.

Adsorption State	Supercell Charge	BN Layer					Graphene Layer			
		$\langle Q_N \rangle$	$\langle Q_B \rangle$	Q_B^*	Q_O	Q_H	$\langle Q_C \rangle$	Q_C^*	Q_O	Q_H
Raw Surface	0	-.35	.35	-	-	-	0	-	-	-
Adsorbed	0	-.35	.35	.17	-.4	.23	0	-.06	-.38	.15
Desorbed	0	-.35	.36	-	-.49	.28	0	-	-.55	.28
Adsorbed	-1	-.35	.33	.13	-.52	.19	-.01	-.06	-.42	.12
Adsorbed	-1	-.35	.45	-	-.98	.24	-.01	-	-.78	.25

Thermodynamics

The relevant thermodynamical quantity evaluated at room temperature (297.15 K) and pressure (the dielectric permittivity of the implicit solvent being chosen equal to the value for water at $P = 1$ bar) is the Gibbs free energy of first adsorption, $\Delta G_{ads1}(T, P)$ defined similarly as the energy of first adsorption :

$$\Delta G_{ads1}(T, P) = G(OH_a) - G(Sub + OH_f), \quad (1)$$

where $G(OH_a)$ is the Gibbs free energy of the system with OH^- adsorbed on the surface and $G(Sub + OH_f)$ is the Gibbs free energy of the system with a free OH^- . We approximate the Gibbs free energy simply as the free energy $A = E - TS$ of the system at temperature T (E is the internal energy and S is the entropy):

$$G = A + PV \approx A \quad (2)$$

since we are in condensed phase and variations of volume are negligible. The situation described is that of the system immersed in liquid water.

For the system with OH^- adsorbed on the surface, we evaluate its free energy using the harmonic approximation as

$$A(\text{OH}_a) = E^{\text{sol}}(\text{OH}_a) + ZPE(\text{OH}_a) - k_B T \log(Q^{\text{vib}}(\text{OH}_a)) \quad (3)$$

with $ZPE(\text{OH}_a) = \sum_i \frac{\hbar\omega_i}{2}$ the zero point energy, k_B the boltzmann constant and

$$Q^{\text{vib}}(\text{OH}_a) = \prod_i \frac{1}{1 - e^{-\frac{\hbar\omega_i}{k_B T}}}, \quad (4)$$

where \hbar is the reduced Planck constant and ω_i are the vibrational frequencies of the system in the harmonic approximation.

The free energy of the system with a free OH^- in presence of the slab is the sum of the free energy of the slab (denoted *Sub*) and that of the free OH^- :

$$A(\text{Sub} + \text{OH}_f) = A(\text{Sub}) + A(\text{OH}_f). \quad (5)$$

The substrate is treated also in the harmonic approximation yielding

$$A(\text{Sub}) = E^{\text{sol}}(\text{Sub}) + ZPE(\text{Sub}) - k_B T \log(Q^{\text{vib}}(\text{Sub})) \quad (6)$$

with $ZPE(\text{Sub}) = \sum_i \frac{\hbar\omega'_i}{2}$ and

$$Q^{\text{vib}}(\text{Sub}) = \prod_i \frac{1}{1 - e^{-\frac{\hbar\omega'_i}{k_B T}}}, \quad (7)$$

where ω'_i are the vibrational frequencies of the slab alone. In the case of the free OH^- there are three extra translational degrees of freedom and a reference should be chosen. As the situation described here is that of a solute, OH^- , in water solution, we take as reference the standard concentration $c^0 = 1 \text{ mol } L^{-1}$. This will be useful in particular in the following to

link the surface coverage to pH. Since OH^- is a non symmetric linear molecule, we have

$$\begin{aligned}
 A(\text{OH}_f) = & E^{sol}(\text{OH}_f) + ZPE(\text{OH}_f) \\
 & - k_B T \log(Q^{stretch}(\text{OH}_f)) \\
 & - k_B T \log(Q^{rot}(\text{OH}_f)) - kT \log(Q^{trans}(\text{OH}_f)),
 \end{aligned} \tag{8}$$

where $Q^{stretch}(\text{OH}_f)$, $Q^{rot}(\text{OH}_f)$ and $Q^{trans}(\text{OH}_f)$ are respectively the vibrational, rotational and translational partition functions. The vibrational partition function is as before

$$Q^{stretch}(\text{OH}_f) = \frac{1}{1 - e^{-\frac{\hbar\omega_{stretch}}{k_B T}}}, \tag{9}$$

where $\omega_{stretch}$ is the O-H stretch frequency, while the rotational partition function for a linear non-symmetric molecule is given by

$$Q^{rot}(\text{OH}_f) = \frac{8\pi^2 I k_B T}{h^2}, \tag{10}$$

where I is the inertial moment of OH^- . At the standard concentration c^0 , the translational partition function becomes

$$Q^{trans}(\text{OH}_f) = \frac{1}{\lambda_D^3 c^0 N_A}, \tag{11}$$

with $\lambda_D = h/\sqrt{2\pi m k_B T}$ the DeBroglie wavelength, m the mass of one OH molecule and N_A the Avogadro constant. Note that since we did not compute the energy of the substrate and the free OH^- separately, we have written $E^{sol}(\text{Sub}) + E^{sol}(\text{OH}_f) = E^{sol}(\text{Sub} + \text{OH}_f)$, where $E^{sol}(\text{Sub} + \text{OH}_f)$ is the energy of the substrate in presence of OH^- in the center of the computation cell.

Values for each thermodynamic contribution computed at $T = 297.15$ K can be found in Table 3. It is noteworthy that the most important correction arises from the ZPE term but since we are dealing with differences to compute ΔG_{ads1} , all minor terms play a role.

More details about this approach can be found in.¹⁻³

Table 3: Detailed thermodynamic corrections and the Gibbs free energy of the first adsorption evaluated in eV at 297,15 K and 1 bar. ϵ_b designates the dielectric permittivity of the solvent, ZPE stands for the zero point energy, Q corresponds to the various contributions to the partition function.

OH^-	BN layer	Graphene layer
T (K)		297.15
ϵ_b ($P = 1$ bar)		78.4
$ZPE(OH_a)$	+ 9.5	+ 10.51
$-k_B T \log(Q^{vib}(OH_a))$	- 0.81	- 0.72
$ZPE(Sub)$	+ 9.19	+ 10.15
$ZPE(OH_f)$	+ 0.23	+ 0.23
$-k_B T \log(Q^{vib}(Sub))$	- 0.72	- 0.61
$-k_B T \log(Q^{stretch}(OH_f))$	- 4.5 10^{-10}	- 4.5 10^{-10}
$-k_B T \log(Q^{trans}(OH_f))$	- 0.19	- 0.19
$-k_B T \log(Q^{rot}(OH_f))$	- 0.25	- 0.25
E_{ads1}^{sol}	- 0.89	+ .33
$\Delta G_{ads}(T, P)$	- 0.46	+ 0.79

References

- (1) Reuter, K.; Scheffler, M. Composition and Structure of the RuO₂(110) Surface in an O₂ and CO Environment: Implications for the Catalytic Formation of CO₂. *Phys. Rev. B* **2003**, *68*, 045407.
- (2) Loffreda, D. Theoretical Insight of Adsorption Thermodynamics of Multifunctional Molecules on Metal Surfaces. *Surf. Sci.* **2006**, *600*, 2103 – 2112.
- (3) Hill, T. *An Introduction to Statistical Thermodynamics*; Addison-Wesley series in chemistry; Dover Publications, 1960.