DFT study of adsorption density of gas molecules in 2D materials

R. Ortega*, L. Donetti, C. Navarro, C. Márquez, F. Gámiz

Nanoelectronics Research Group, CITIC-UGR,Universidad de Granada, Granada, Spain

Gas sensors are required in many fields, such as city air quality and emission, environmental monitoring or medical diagnostics [1]. 2D materials have become promising candidates to produce highly sensitive gas sensors due to their extraordinary properties [2], but they suffer from the disadvantage of having complicated manufacturing processes. Due to this inconvenience, it would be desirable to know, before fabrication, how well a specific 2D structure (monolayer, multilayer or a heterostructure) is going to perform in sensing a specific gas molecule. With this aim in mind, a modified version of the Langmuir adsorption model (derived from Statistical Mechanics, assuming non-localized adsorption) [3] coupled to Density Functional Theory (DFT) calculations has been developed to compute the density of adsorption of molecules in 2D structures. As an example of application NH_3 and N_2 adsorption in MoS_2 monolayer has been investigated, but the model is not limited to these systems.

First, in order to justify the hypothesis made in the model development, the height of the barriers that molecules experience when moving across the MoS_2 plane have been calculated. It can be seen in Figure 1 how the average thermal energy of NH_3 molecule at 300K is significantly larger than the height of the barriers, and the same behavior is observed for N_2 therefore, it is justified to assume that the molecules can move in the plane.

Numerous structural relaxations have been performed using DFT and the L-BFGS optimization algorithm as implemented in QuantumATK [4]. From these calculations, two preferred points for adsorption have been extracted for both molecules, referred to as 'center' and 'Mo' as shown in Figure 2. To study the orientations in which the molecules are adsorbed, ab-initio simulations have been performed to extract the interaction energy between the molecules and the monolayer of MoS_2 as a function of the angle between them (Figure 3a). In the case of NH_3 a single preferred configuration has been found, that with the hydrogen plane parallel to the monolayer (Figures 2a and 2c). This can be deduced by the fact that exist a single angle that significantly minimizes the interaction energy. For N_2 it has been extracted similar results, finding that most stable configuration is that in which N_2 line form an angle of 56° with the MoS_2 plane (Figure 2b and 2d).

Using the information obtained about the adsorption process, the density of adsorption of NH_3 and N_2 in a MoS_2 monolayer has been calculated applying the modified Langmuir model. From that model it can be deduced that [3]

$$\rho = \frac{N}{A} = \frac{p}{k_B T}\left(\frac{2\pi k_B T}{h^2}\right)^{-\frac{1}{2}}\left[\exp\left(\frac{-E_{ads}}{k_B T}\right)\sum_{n=0}^{\infty}\exp\left(\frac{-E_n}{k_B T}\right)\right],$$

where N is the number of adsorbed molecules, p is the partial pressure of the gas, E_{ads} is the depth of the potential well obtained in the interaction curves (Figure 3b), and E_n are the eigenvalues of the potential well (harmonic oscillator) in which the molecules are trapped. The obtained values for the two

* Corresponding author: email: rubenortega@ugr.es

preferred adsorption sites, in the most probable orientation, are $\rho = 2.004 \times 10^{15}\, cm^{-2}$ in the case of NH_3 and $\rho = 2.513 \times 10^{13}\, cm^{-2}$ in the case of N_2 for T= 300 K and p = 1 atm. The variation of ρ with temperature has been calculated too, as can be seen in Figure 3c for NH_3 and Figure 3d for N_2.

The interaction between the monolayer MoS_2 and the NH_3 and N_2 molecules have been investigated with first principles calculations and the density of adsorption has been computed using a statistical mechanics-based model. We obtain that MoS_2 is ~80 times more sensible to NH_3 than N_2, a result consistent with the fact that N_2 is an inert gas.

This work paves the way for conducting new calculations employing different molecules and structures to determine the optimal sensing structure for detecting specific molecules.

References

[1] N. Nasiri et al., "Nanostructured gas sensors for medical and health applications: low to high dimensional materials, *Biosensors*, 9 43, 201, [2] N. O. Weiss et al., "Graphene: An emerging electronic material", *Advanced materials*, 24, 5782-5825, 2012, [3] T. Hill, "An introduction to statistical thermodynamics",2nd edition, Dover Publications Inc, 2003, [4] QuantumATK version V-12.2023, Synopsys QuantumATK.

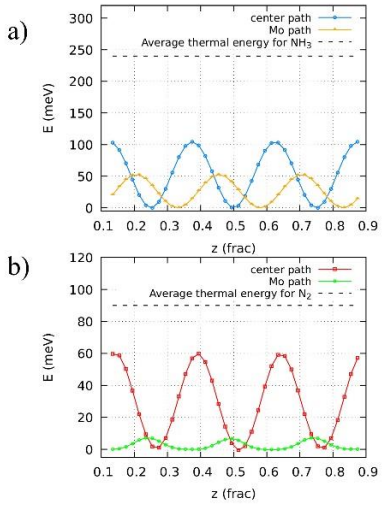

Figure 1. Potential barriers experienced by NH_3 a) and N_2 b) when moving across MoS_2.

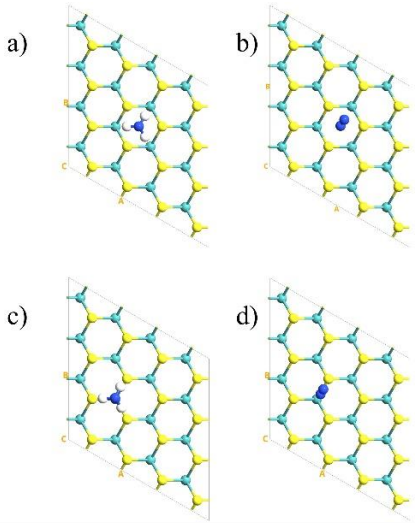

Figure 2. Center adsorption sites a) and b), and Mo adsorption sites c) and d).

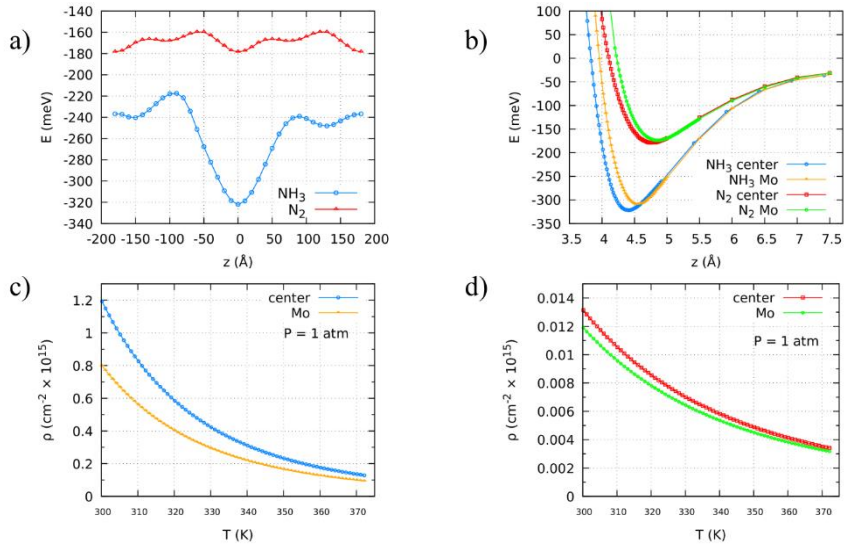

Figure3. Interaction energy as a function of the angle a) and vertical distance b) between the molecules and MoS_2, and variation of ρ with temperature for NH_3 c) and N_2 d).