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Molecular dissociation in a defected MoS_2 monolayer

Transition-metal dichalcogenides have attracted great attention at both fundamental and technological levels. Among them, the most widely studied material is the MoS_2. While its bulk shows a semiconductor character with indirect gap, one single layer presents a direct one [1]. This very interesting property can be exploited in nano-opto-electronics or spintronics applications [2].

Two dimensional (2D) materials are generally known as poorly reactive and following this idea, many authors have fabricated transistors using MoS_2 monolayers in order to test their application in a gas sensor device [3]. Indeed, physisorbed molecules on the MoS_2 monolayer can modify its electronic properties and thus the electronic current is altered in the transistor, leading to the molecular detection. The reactivity of MoS_2 is enhanced in the defected monolayer [4].

Here, we have theoretically studied the adsorption of different molecules on the pristine and defective MoS_2. Using the Density Functional Theory (DFT) VASP code [5], we have found that molecules can be physisorbed at typical van der Waals (vdW) distances, chemisorbed forming a bond with the atoms in the defected MoS_2 or even dissociated in different situations [6]. In Fig.1 three examples are shown: a CO_2 molecule adsorbed over the pristine MoS_2, a CO molecule bonded to the Mo atom in a S antisite and the dissociation of a NO_2 molecule on the same defect.

The dissociative process presented in Fig. 1c) is obtained at 0 K temperature when no energy barrier has to be overcome. Alternative cases have been analyzed using the Nudge Elastic Band (NEB) method implemented in VASP. Fig. 2 shows a concrete example: the CO_2 dissociation on a S vacancy. Starting from the molecule physisorbed over the vacancy, it jumps an energy barrier of +0.28 eV in the approach to the vacancy site and finally, one O atom occupies the empty hole and a CO molecule moves away to a position on a perfect area. Finally, we have performed *ab initio* Molecular Dynamics (MD) simulations [7] at different temperatures on other alternative molecular dissociations in order to understand the atomic movements in such processes.

References

[1] K. F. Mak, C. Lee, J. Hone, J. Shan and T. F. Heinz, Phys. Rev. Lett., 105, (2010), 136805.

[2] B. Radisavljevic *et al.*, Nat. Nanotechnol., 6, (2011), 147; Q. H. Wang, *et al.*, Nat. Nanotechnol., 7, (2012), 699.

[3] B. Liu, Chen, G. Liu, A. N. Abbas, M. Fathi and Ch. Zhou, ACS Nano, 8, (2014), 5304.

[4] C. González, *et al.* J. Phys. Chem. C, 120, (2016), 17115-17126.

[5] G. Kresse and D. Joubert, Phys. Rev. B, 59, (1999), 1758.

[6] C. González *et al*. J. Phys. Chem. C (Submitted)

[7] J. Lewis, *et al* Phys. Status Solidi B, 248, (2011), 1989-2007.

Figures

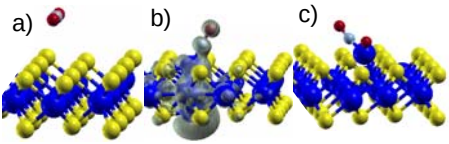

Figure 1: The three alternative situations when a molecule is adsorbed on a MoS_2 monolayer: a) a CO_2 molecule physisorbed on the pristine layer, b) a CO molecule bonded to a Mo atom occupying a S vacancy and c) a NO_2 molecule dissociated.

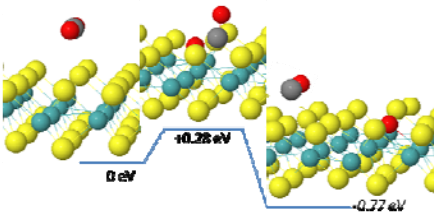

Figure 2: Energy barrier of the CO_2 dissociation in a S vacancy.