

Crossing of H/H⁺ through hydrogenated/protonated graphene prototypes: A new cooperative mechanism

M. I. Hernández^{1*}, J. Campos-Martínez¹, M. Bartolomei¹, R. Hernández-Lamoneda²

¹Instituto de Física Fundamental (IFF-CSIC), C/ Serrano 123, Madrid 28006, Spain

²Centro de Investigaciones Químicas, Univ. Autónoma del Estado de Morelos, 62210, Cuernavaca, Mor, Mexico

*marta@iff.csic.es

This work has been initially motivated by the experimental observation that proton permeation through graphene involves a low activation energy (~0.8 eV)[1], a discovery that contrasted with the common belief that this material is completely impermeable to all atoms under ambient conditions. A possible explanation involves the flipping of a chemisorbed proton from one to the other side of the graphene layer but the related energy barrier is too high (3.5 eV). In this work[2] we have found that this barrier can decrease to the 1.0-1.5 eV range if graphene is assumed to be initially protonated at high local coverage. For this purpose, DFT (PBE/cc-pVTZ) calculations were conducted (exploiting circumcoronene and circumcircumcoronene as graphene prototypes) for an increasing number of protons chemisorbed along a given carbon ring. As seen in Fig.1 (for a five-times protonated carbon ring), the proposed permeation mechanism involves the insertion of the flipping proton into the middle of an effectively broken C-C bond, a linkage that is restored in the products configuration, in analogy with processes originally reported for carbon nanotubes[3].

We believe that these findings can help to rationalize the proton permeation observations since, despite progress[4], theoretical insight is not complete or satisfactory yet. In addition, they can provide clues about properties of hydrogenated graphene as well as about astrochemical processes involving hydrogen and large PAHs[5]. To this end, preliminary results on related processes involving neutral atomic hydrogen will be also reported.

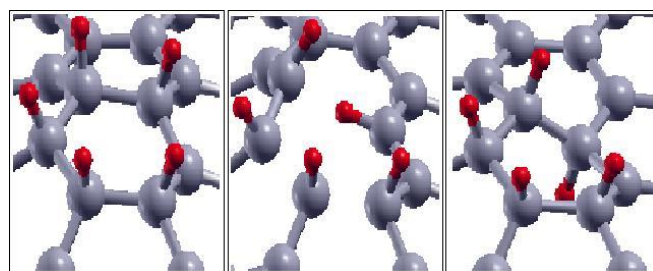


Fig. 1: Proton flipping through 5-times protonated circumcoronene. Left, central and right panels: the stationary point geometries of the reactant, transition and product states, respectively. The activation energy is about 1.5 eV.

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References

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