

A new cooperative mechanism for the permeation of H/H⁺ through hydrogenated/protonated graphene

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The common belief that graphene is completely impermeable to all atoms under ambient conditions has been recently questioned since a low activation energy (~0.8 eV) has been experimentally measured[1] for the proton permeation through the carbon 2D material. 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 down to the 1.0-1.5 eV range if graphene is assumed to be initially protonated at high local coverage. For this purpose, suitable DFT calculations were conducted, by exploiting graphene finite prototypes, for an increasing number of protons chemisorbed along a given carbon ring. As shown 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 proposed for carbon nanotubes[3].

We believe that present 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 hydrogen are also reported.

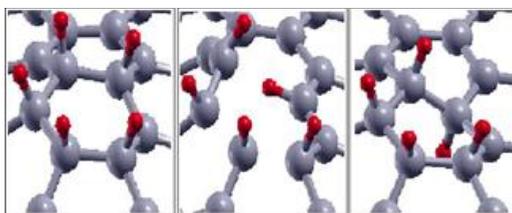


Fig. 1: Proton flipping through a 5-times protonated graphenic ring. Left, central and right panels: the stationary point geometries of the reactant, transition and product states, respectively. The activation energy is about 1.5 eV.

References

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