

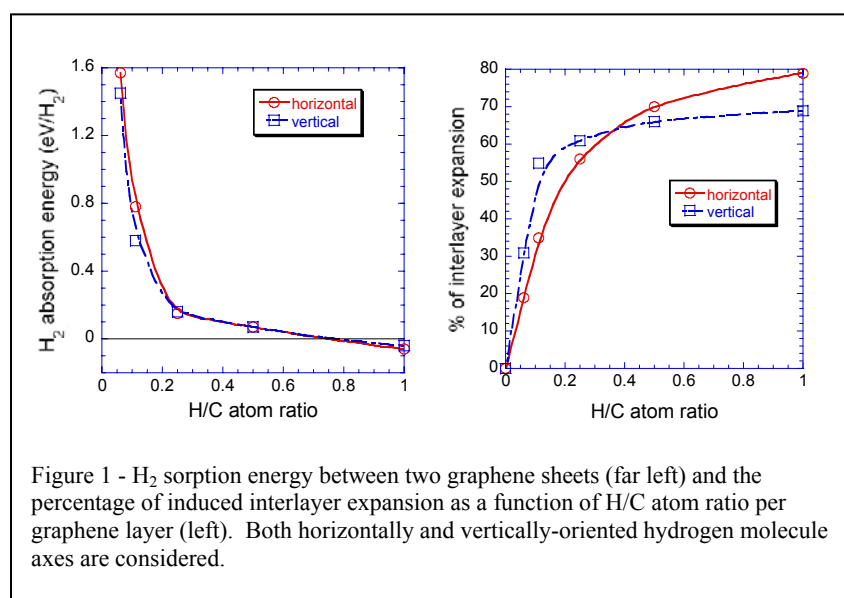
## Theoretical Investigation of the Energetics of Hydrogen Interaction with Graphene Layers: the Effect of Interlayer Spacing on Hydrogen Storage

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This theoretical effort is part of the project entitled “Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbon”. The objective is to understand the interactions of hydrogen with graphite-like structures and the role of metal particles on the intercalation of hydrogen on graphene surface.

Although the carbon layers are normally stacked too closely together for hydrogen molecules to fit between graphene sheets, it is believed that high concentration of H<sub>2</sub> molecules can still be sorbed in the graphite lattice. This is based upon first-principles calculations for the dependence of H<sub>2</sub> sorption energy and graphite interlayer spacing on H<sub>2</sub> molecular sorption between two graphene sheets (Figure 1). Although it is highly energetically unfavorable to exist between the graphene sheets, a large number of H<sub>2</sub> molecules can have low sorption energy due to their ability to induce a dramatic expansion of the graphite interlayer spacing. It is also observed that both H<sub>2</sub> sorption energy and graphite interlayer spacing show a non-linear dependence on hydrogen concentration; a substantial decrease in the H<sub>2</sub> sorption energy together with a significant expansion in the graphite interlayer spacing actually occurs within a very narrow H/C atom ratio.

The results suggest that the major barrier in limiting the amount of hydrogen storage in the graphite lattice comes during the initial uptake stage. Thus, it is possible to achieve high

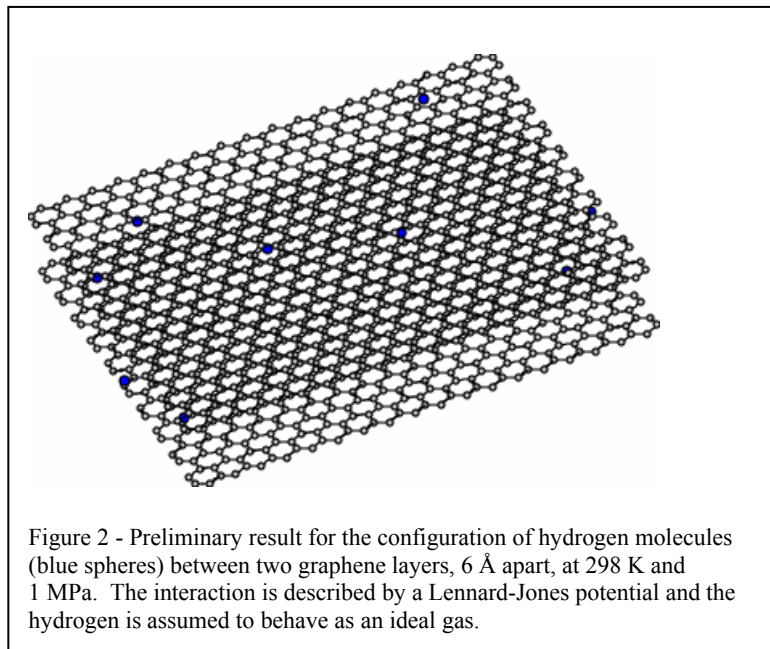


hydrogen storage if the difficulty associated with high H<sub>2</sub> sorption energy at the initial sorption stage can be overcome. It is thought that the initial sorption stage is where the presence of metal particles can be beneficial. A metal particle could play the role that not only expands graphite interlayer spacing but provides chemical interaction that lowers the sorption energy of H<sub>2</sub> molecules adjacent to the metal particles. Once these “initial” H<sub>2</sub> molecules are intercalated, further lattice expansion is induced (Figure 1). An expanded lattice would encourage further hydrogen intercalation. The intercalated H<sub>2</sub> molecules reach a lower energy state as the concentration of H<sub>2</sub> becomes saturated.

Although preliminary results shown in Figure 1 already indicate the formation of a stable state for H<sub>2</sub> molecules between the graphene sheets, it is unclear if this level of H<sub>2</sub> sorption energy is too small for room temperature sorption/desorption. The sorbed H<sub>2</sub> molecules still have

their rotational and stretching degrees of freedom between the graphene sheets. An effective approach to study the temperature and pressure effect on the sorption is to use the grand canonical Monte Carlo (GCMC) method. The technique allows for the determination of the distribution of intercalated particles at a given chemical potential, temperature and volume.

Shown in Figure 2 is the result of a preliminary calculation, using an ideal gas approximation. In the simulation, the interaction of hydrogen molecules with the carbon lattice



is described by a Lennard-Jones potential [*J. Low Temp. Phys.* **41** (1980) 611] and the hydrogen-hydrogen molecular interaction is described by the Silvera-Goldman potential [*J. Chem. Phys.* **69** (1978) 4209]. The amount of hydrogen uptake shown in Figure 2 is lower than the amount observed in experiments. The discrepancy may be due to the fact that the initial model does not accurately describe the dependence of interlayer spacing on hydrogen concentration. One of the goals of the theory effort is to develop a set of potential energy parameters that can properly describe the interaction of hydrogen in

nanostructured carbons such as these graphene layers, based on the results of first-principles calculations.

The model proposed in the study is fully atomistic, which allows for the study of local structural changes in the graphene lattice. First-principles calculations will be used to complement the simulation results and to obtain a detailed understanding of the change in behavior due to localized structural modifications. The GCMC approach will also be implemented to examine the effect of porosity on the hydrogen sorption. Existing models of activated carbon include “slit nanopores,” which are described by missing regions in the graphene sheets. Clearly, such regions provide pre-existing conditions for expanded interlayer distance that can favor hydrogen sorption. The structure, density, and size of such pores will clearly affect the uptake of hydrogen, and part of the experimental characterization will focus on determining these parameters, as well as the general description of the activated carbon with and without metal additions. The favorable formation of dense hydrogen between the graphene sheets, as shown in Figure 1, may cause hysteresis in the curves. Studying this process may help identify barriers to repeated charging/discharging cycles necessary for practical hydrogen storage.