PRF# 57236 – ND 6
Project Title: Unraveling the Interactions between Molecular Species and Two-Dimensional Materials
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The main goal of this project is to present a fundamental study of the mechanisms of molecular interactions with holey 2D structures with a variety of hole sizes as well as passivating chemical groups. Over the past year the research focus related to this grant has been placed on two main areas. The first are deals with Density Functional Theory calculations to understand if a specific interaction is present between a variety of terminations of a graphene model and H_2 and CO_2 molecules. The second area of research was focused on Molecular Dynamics simulations to estimate the self-diffusion coefficient of these two species in graphene. Below, we elaborate on our findings in these areas.

1. *Specific interactions of H_2 and CO_2 with graphene*

In order to study the interaction of graphene with specific molecules in the presence of edges (or holes), we chose circumcoronene as a model system. One passivating H atom from the edge of circumcoronene was replaced by different oxygen containing groups (R=COH, COOH, and OH) representing possible terminations of edge regions around holes in graphene oxide. For H_2 and CO_2 adsorption on the pristine as well as the R-terminated models, we optimized the structures and calculated the zero-point energy (ZPE) corrections using the dispersion corrected B97D3 functional.[1] Besides the interaction on the basal plane for the pristine model, we considered two adsorption positions around the R-substituted edge as shown in Figure 1 for R=COOH. In Table 1 we present our ZPE corrected results. It is interesting to mention that for H_2 our calculated value is in very good agreement with previous calculations[2] as well as experiments.[3] As seen in Table 1, H_2 interaction in all positions is weaker than CO_2. However, the strength of the interaction in either case is highest in the basal plane than at the edges where we observe no significant effect of the termination groups. These results indicate that separation of gases due to specific interaction with molecular species will not work efficiently and if there is a separation effect it will be mostly related to diffusive properties of a given molecular species with respect to another.
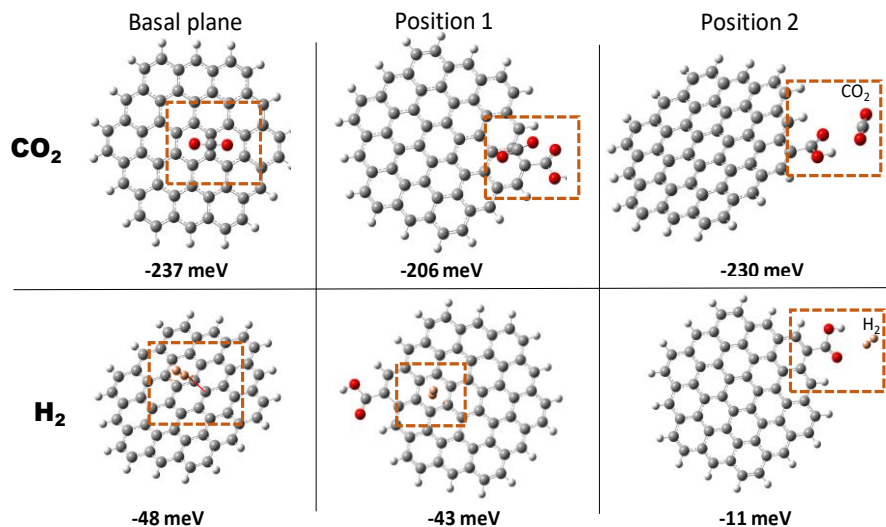

Figure 1: Optimized structures for H_2 and CO_2 adsorption on circumcoronene and R=COOH substituted circumcoronene. Interaction energies for each configuration are shown below each structure. The boxed region represents the interaction region.

Summary: *Our calculations indicate that there is no selective interaction for either H_2 or CO_2 molecules when they adsorb at the edge region or in the basal plane of graphene. In future work, we will look at the strength of these interactions when a metal particle such as Pd is attached at the edges.*

Table 1: Calculated ZPE corrected interaction energies for H2 and CO2 adsorption in model system in different positions (in meV).

R	H$_2$		CO$_2$	
	Pos. 1	Pos.2	Pos. 1	Pos.2
COOH	-43.2	-11.4	-206.5	-230.0
COH	-31.7	-9.3	-210.9	-173.3
OH	-33.7	-13.3	-201.9	-201.9
	basal plane			
H	-48.0		-236.9	

2. Self-diffusion coefficients for molecular species on graphene

Given the importance that diffusion properties of gases have in relation to gas separation we began an investigation of parameters and systems that can be explored using molecular dynamics techniques. As we can see in Table 1, the nature of the interaction between graphene and the studied molecules is dominated by van der Waals forces. Therefore, it might be useful, to test semi-empirical approaches in combination with empirical dispersion to treat this problem. To this end, the ADMP methodology[4] was employed in combination with the PM6D3[5,6] method as implemented in Gaussian 09. Our first task, was to initiate the development of a script that can actually extract data from the ADMP simulations and performs the corresponding time averages in relation with diffusion properties. To this end, mean square displacements (MSD) for the gas molecule of interest need to be calculated. Following Einstein's theory, the diffusion coefficient can be obtained as $D = \lim_{t \to \infty} \frac{1}{4t} \langle |(\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = \lim_{t \to \infty} \frac{1}{4t} MSD$. This code is being finalized by one of the undergraduate students in the group and will be then tested in a model systems as part of the student's senior research project.
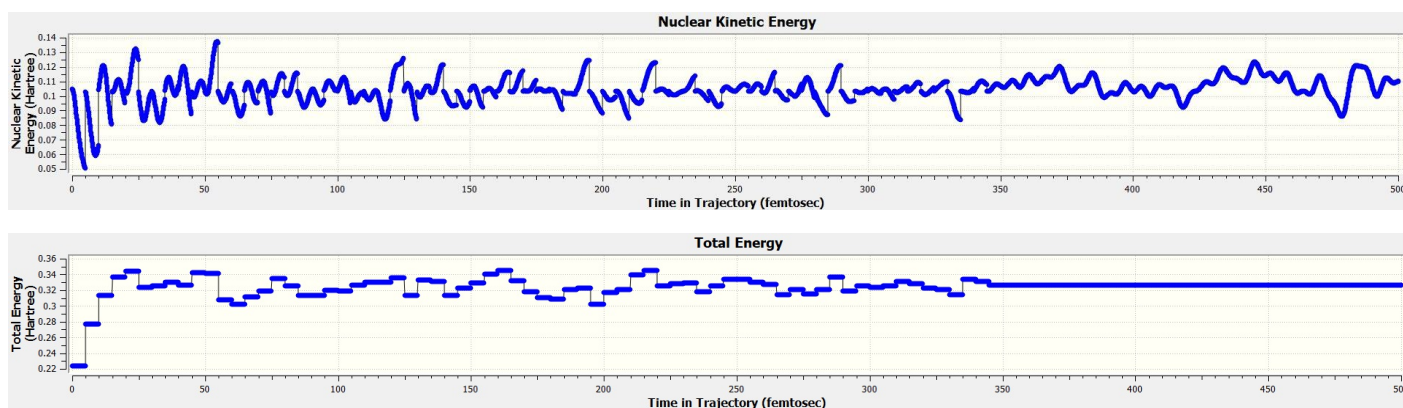

Figure 2: Example of MD thermalization and diffusion of CO2 on a graphene model.

Additionally, a master student has been working on calibrating the thermalization of the MD simulations which has been part of his MS dissertation which has been successfully completed in the Summer of 2018. An example of such calibration is shown in Figure 2, where the system is forced to room temperature every 5 femtoseconds for 350 femtoseconds and then is let to evolve. The maximum variation of total energy after thermalization is 1.2 10^{-5} Hartree.

Summary: *A python script is being finalized to handle the output information from a Gaussian 09 MD/PM6D3 simulation to calculate diffusing molecule MSDs to obtain the self-diffusion coefficients of gas species adsorbed on graphene.*

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