

Accurate and Efficient Calculation of the Desorption Energy of Small Molecules from Graphene

S. Conti and M. Cecchini*

Laboratoire d'Ingénierie des Fonctions Moléculaires ISIS, UMR 7006 CNRS,
Université de Strasbourg, F-67083 Strasbourg Cedex, France

*Corresponding author: mcecchini@unistra.fr

Understanding the energetics of molecular adsorption at nanostructured carbon materials opens up to outstanding applications in the postgraphene era. The accurate determination of the adsorbate binding affinity remains however a challenging task both experimentally and computationally. In this work, we report on the determination of the desorption energy of 25 chemically diverse compounds from graphite using computational methods at different levels of theory: empirical Force Fields (FF), Semiempirical Quantum Mechanics (SQM), and Density Functional Theory (DFT). By comparing the computational predictions with literature Temperature Programmed Desorption (TPD) experiments we found that the dispersion corrected semiempirical method PM6-DH+ yields desorption energies in quantitative agreement with experiments with an average error of $1.25 \text{ kcal mol}^{-1}$, see Fig. 1a.

The discovery of a fast and accurate approach to molecular adsorption at surfaces prompted us to search the chemical space of the adsorbate to optimize the binding affinity for graphene. We found that polarizable groups containing sulfur and halogens atoms significantly enhance the interaction strength with the substrate. In particular, we predict that perchlorination of aliphatic hydrocarbons doubles the desorption energy from graphene in vacuum; see Fig. 1b. The efficiency of the PM6-DH+ calculations, which allows for screening libraries of compounds, guided the design of potentially improved graphene surfactants, which are commercially available. [1]

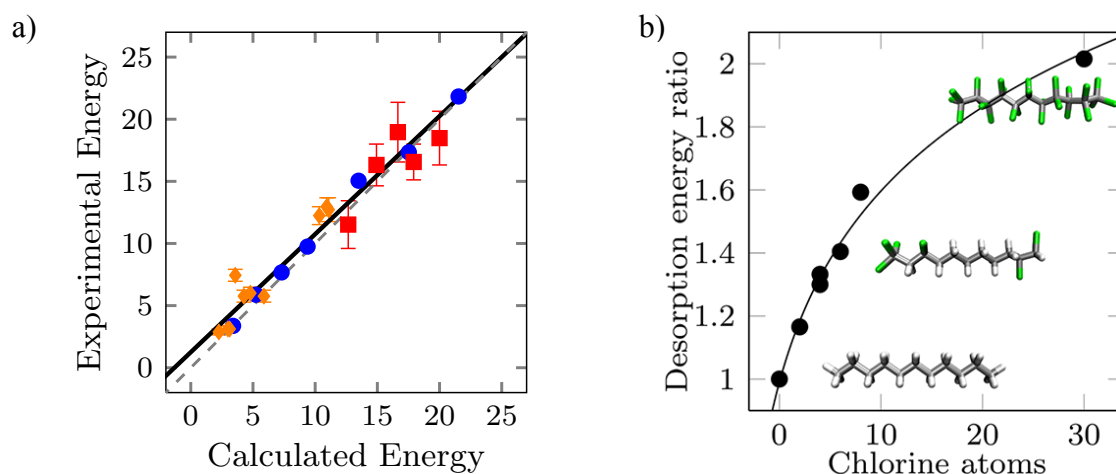


Figure 1: a) Correlation between the experimental and calculated desorption energy from graphene using the PM6-DH+ semiempirical method. The different colors represent different classes of molecules: alkanes in blue, aromatic compounds in red, and small molecules in orange. The fit is clearly very close to the ideal one to one correlation (dashed line). b) Effect of chlorination on undecane. The ratio between the desorption energy of partially chlorinated molecules and undecane is plotted as a function of the number of chlorine atoms added. While full chlorination allows a two-fold increase in the affinity for the surface, even partial chlorination with only 8 chlorine atoms significantly increase the desorption energy (up to 60%).

Motivated by the computational predictions, the adsorption energy on graphite of coronene ($C_{24}H_{12}$) was compared to that of its perchlorinated analog ($C_{24}Cl_{12}$) by temperature programmed desorption (TPD) in ultra-high vacuum in collaboration with the group of Manfred Kappes at KIT (Karlsruhe). The results show a significant increase in the desorption temperature for the chlorinated derivative of 47 K, which corresponds to an increase in the desorption energy of about 5 kcal mol^{-1} ; see Fig. 2a. In addition, the use of perchlorinated versus hydrogenated coronene as dispersion-stabilizing agent in liquid-phase exfoliation of graphite was explored in collaboration with the group of Paolo Samori at ISIS (Strasbourg). The result show that perchlorination improves the quality of the dispersed graphene, increasing the yield of single over multiple layers graphene sheets as shown by HRTEM; see Fig 2b. Consistently, micro Raman analysis of centrifuged graphene dispersions showed an increase in the percentage of monolayers from 36% with coronene, to 51% with perchlorocoronene. [2]

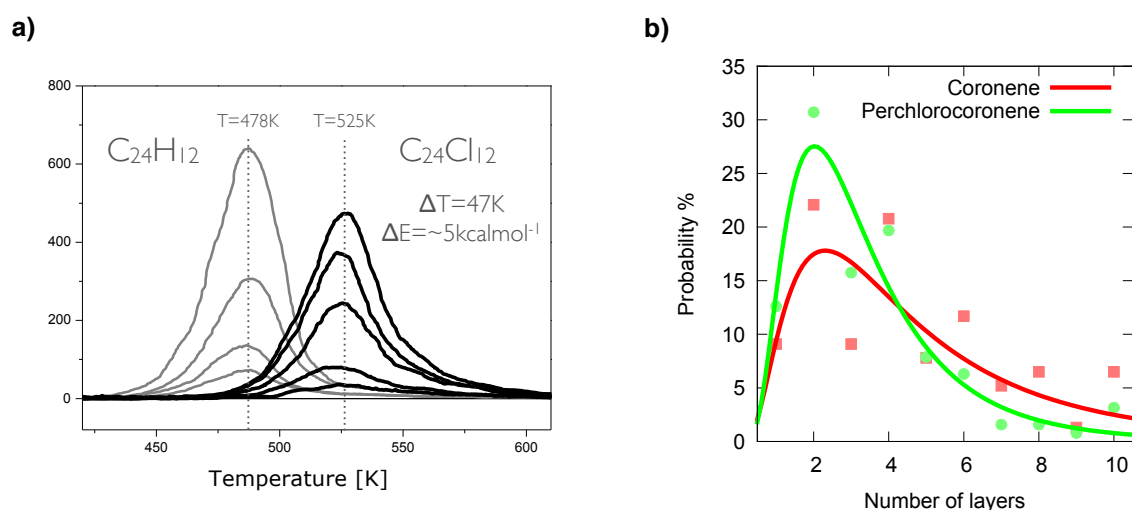


Figure 2: a) TPD of coronene and perchlorocoronene from graphite. The clear shift to higher temperatures of 47K for the desorption peak of the chlorinated compound indicates a significant increase in the desorption energy of about 5 kcal mol^{-1} . b) Distribution of graphene flakes obtained upon liquid phase exfoliation with coronene in DCB (red), and perchlorocoronene in DCB (green). It is apparent how the use of the chlorinated surfactants enhances the formation of monolayers, decreasing significantly the formation of flakes of 7 or more layers.

In conclusion, low-cost computational methods were found to be useful to explore the Chemistry on graphene. Our joint computational and experimental results demonstrate that chlorine substitution significantly increases the binding affinity of small molecules for graphene. By taking advantage of the enhanced adsorbate/substrate interaction energy archived by perchlorination, we developed from first principles an improved dispersion stabilizing agents for the liquid phase exfoliation of graphite. [3]

References

- [1] S. Conti and M. Cecchini, *J. Phys. Chem. C*, 2015, 119 (4), pp 1867–1879.
- [2] A report on desorption energy predictions, TPD and exfoliation experiments is under preparation.
- [3] This work was financially supported by the Agence Nationale de la Recherche through the LabEx Project CSC. S.C. received support from IdeX Investissements d’Avenir (Grant No. 16141). Financial support from the International Center for Frontier Research in Chemistry (icFRC) is gratefully acknowledged. The work was granted access to the HPC resources of [CCRT/CINES/IDRIS] under the allocation 2014-[076644] made by GENCI (Grand Equipement National de Calcul Intensif).