

Non-covalent Interactions of Small Organic Molecules To Graphene: Theory and Experiment

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Abstract

Graphene is a two-dimensional π -conjugated material having extraordinary physical properties, which makes it a perspective material in catalysis, energy storage, nano(opto)electronics and sensor applications.[1,2] The application potential of graphene can be enormously enhanced by its covalent and non-covalent functionalization.[3] An exact quantification of interaction between graphene and guest molecules as well as thorough understanding of the nature of interaction between graphene and guest molecules have not been yet achieved. We measured the adsorption enthalpies of acetone, acetonitrile, dichloromethane, ethanol, ethyl acetate, hexane, and toluene vapours on graphene by inverse gas chromatography. The measured adsorption enthalpies ranged from -5.9 kcal/mol for dichloromethane to -13.5 kcal/mol for toluene. We compared the experimental data with theoretical calculations at density functional theory (PBE, B97D, M06-2X, and optB88-vdW), wave function theory (MP2, SCS(MI)-MP2, MP2.5, MP2.X, and CCSD(T)), and empirical (OPLS-AA) levels using two graphene models: coronene and infinite graphene (using periodic boundary conditions). We also employed symmetry-adapted perturbation theory (SAPT) calculations to understand the nature of interaction between graphene model (coronene) and the organic molecules. SAPT calculations showed that the interactions were governed by London dispersive forces (amounting to 60% of attractive interactions), even for the polar molecules. The theoretical calculations also showed that the adsorption enthalpies were largely controlled by the interaction energy. Adsorption enthalpies obtained from ab initio molecular dynamics employing non-local optB88-vdW functional were in excellent agreement with the experimental data, indicating that the functional can cover physical phenomena behind adsorption of organic molecules on graphene sufficiently well.[4] We further used theoretical calculations to understand changes in adsorption enthalpies of acetone to graphene and graphite with surface coverage.

References

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