Abstract

Quantification and understanding of the interaction of adsorbed molecules with graphene represents a challenging topic in non-covalent functionalization of graphene.[1, 2] We measured adsorption enthalpies of organic molecules (acetone, acetonitrile, dichloromethane, ethanol, ethyl acetate, hexane, and toluene) to graphene by inverse gas chromatography. We also calculated the adsorption enthalpies by various theoretical methods including 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 calculations (OPLS-AA) using two graphene models: coronene and infinite graphene. We calculated the adsorption enthalpies also from ab initio molecular dynamics employing non-local optB88-vdW functional. Comparison of theoretical calculations with the experimental data indicates that the optB88-vdW functional can cover physical phenomena behind adsorption of organic molecules on graphene sufficiently well, is computationally affordable and can be recommended for calculation on non-covalent interactions to graphene. It is also worth noting, that the empirical potential (OPLS-AA) may be used at least for semiquantitative estimations and is applicable for studies on large complex systems involving graphene. The symmetry-adapted perturbation theory (SAPT) calculations indicated that the interactions of organic molecules to graphene were governed by London dispersive forces (amounting to 60% of attractive interactions), even for the polar molecules. The results also showed that the adsorption enthalpies were largely controlled by the interaction energy.[3]

Keywords: graphene, surface energy analysis, iGC, DFT, SAPT

LITERATURE


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