4E01

グラフェン表面上におけるイオン液体構成イオンの相互作用に関するベンチマーク計算

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Ionic liquids (ILs) are known as salts with melting point below 100 ˚C due to their molecular composition consisting of a bulky organic cation and an inorganic anion. Their characteristic properties and potentials allow to be widely applied to various research fields such as material science and green chemistry. Recently, it became possible to monitor the contact of ILs on solid surface or the confinement in nanospace of single walled carbon nanotubes (SWCNTs) [1]. However, many aspects of such systems (e.g. aggregation process and phase transition behavior) are not yet fully understood. Aiming at molecular dynamics simulations of ILs-SWCNTs systems more accurate than those based on computationally inexpensive classical force fields (where surface polarization is often not included), we performed as a first stage quantum chemical benchmark calculations for multiple model systems composed of graphene flakes and typical ionic liquids components.

As a prototypical IL compound, 1,3-dimethylimidazolium cation ($C_5H_9N_2$, [dmim+] for abbreviation) and nitrate anion (NO_3^-) are chosen. At the beginning, the complexes are constructed by placing each IL component above the central hexagonal ring of four graphene flake models; benzene (C_6H_6), coronene ($C_{24}H_{12}$), circumcoronene ($C_{54}H_{18}$), and dicircumcoronene ($C_{96}H_{24}$). The compounds are classified according to 6 different IL orientations with two basic motives – one where the cation or anion is roughly parallel to the graphitic surface (2 structures), the other where the plane is perpendicular (4 structures) (see Figure 1).
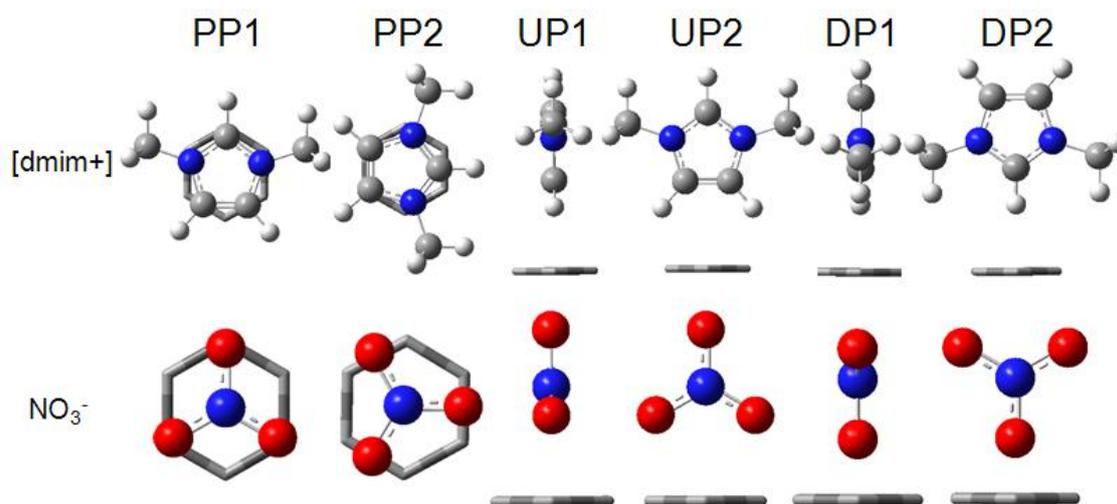

Figure 1. Constructed complexes by IL components and graphene flakes. Only the central hexagonal ring is shown, and is positioned underneath the IL components.

The model complexes were optimized using 3 different levels of theory – RI-MP2/SVP (diffuse functions were manually added for only ILs components), SCC-DFTB-D (dispersion augmented self-consistent-charge density-functional tight-binding) [2], and OPLS-AA force field where the IL

parameters were taken from reference [3-4]. Regarding the molecular structure, it was observed that the intermolecular distance becomes shorter and the SCC-DFTB-D intermolecular distances are close to those of RI-MP2/SVP as the size of graphite becomes larger, while OPLS-AA tends to estimate longer intermolecular distance compared with others.

Then, single point calculations were performed to evaluate the interaction energies for optimized geometries. *Ab initio* and DFT with dispersion methods (RI-(SCS)-MP2, LC-BOP+ALL, M06-2X, etc.) with SVP and TZVPP basis sets were used for comparison with the SCC-DFTB-D and OPLS-AA methods. The influence of basis set superposition error (BSSE) was evaluated by performing Boys-Bernardi counterpoise correction. For LC-BOP+ALL, two different μ values (0.330 and 0.470) were tested. Several selected results are shown in Figure 2. It was obvious the bad performance of OPLS-AA, the order of orientation stability, and the graphite size dependency. Although the current SCC-DFTB-D method demonstrates the moderate agreement with the high-level quantum chemical methods especially for [dmim+] system, the results of NO_3^- system varies strongly with the employed methods. Therefore, we plan to improve the DFTB repulsive potentials and the dispersion energy terms using high-level benchmark data as target.
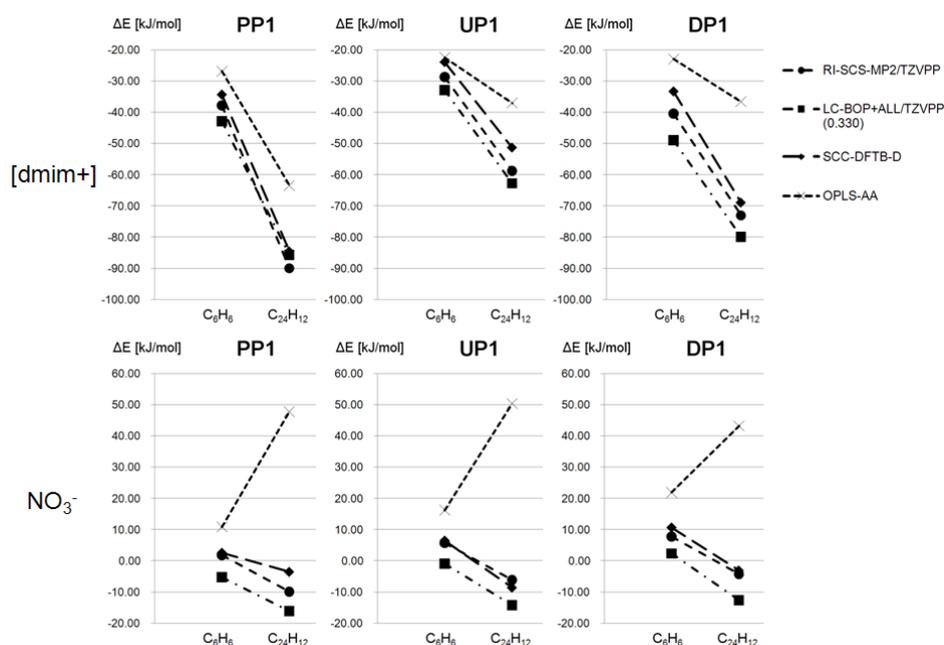

Figure 2. Interaction energies of model complexes optimized with RI-MP2/SVP.

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