A theoretical study on physisorption states of non-metal adatom on graphene

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Because of the low density of gases in cosmic space, molecular formation reaction can not release the heats of exothermal chemical reactions. On the other hand, if the chemical reaction occurs on dust grain surfaces, heat of formation can be dissipated to substrates. Therefore, dust grains are considered as one of the most important stages for various molecular formation reaction.[1] Dust grains are generally in low temperature condition. For instance, the temperature of dense clouds is about 10 K. In these low temperature conditions, adsorbates cannot thermally diffuse because of its strong chemical bonding to substrates, which indicates that the physisorbed adsorbates play an important role of chemical reaction on dust grain. Therefore, in this study, we investigated the physisorption properties of non-metal atoms on carbon materials.

In this study, we performed the first principles calculations based on density functional theory, which is implemented in the plane-wave and projector-augmented wave method code, the Vienna Ab-initio Simulation Package (VASP 5.3.3).[2-7] We applied a 550 eV cutoff to limit the plane-wave basis set without compromising computational accuracy. A 5 × 5 × 1 Monkhorst–Pack special k-point grid [8] for the first Brillouin zone sampling and a Gaussian smearing model of σ=0.05 eV was used. Moreover, we took the van der Waals interaction into consideration with the non-local correlation functional rev-vdW-DF2 [9,10] to treat pysisorption states on graphene accurately. We focused on the H, N, and P adsorption on 4 × 4 graphene. The supercell was constructed with a 20 Å vacuum separation between slabs to reduce the interaction between slabs.

At first, we studied the dependence of H adsorption energy on the H coverage. We considered the H coverage of 0.02 to 1 ML. We found that the interaction between H atoms on graphene is smaller than 1 meV with H-H distance of 10 Å. Therefore, in this study, we adopted 4x4 graphene as substrates. The adsorption energies of H, N, P atoms on graphene correspond to 80, 120, 130 meV, respectively. In the workshop, we will also report the diffusion properties of adsorbates on graphene.

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