§18. Chemisorption of Hydrogen on Graphite (0001): Spin-Polarized Density-Functional Tight-Binding Molecular Dynamics Simulations Using G2MS-Derived C-H Parameters

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Original self-consistent-charge density-functional tight-binding (SCC-DFTB) potential energy curves (PECs) for the hydrogen chemisorption on a central carbon atom of pyrene and coronene molecules are qualitatively wrong compared to those predicted by hybrid DFT (B3LYP/cc-pVDZ), *ab initio* (RCCSD(T)/cc-pVDZ), and G2MS levels of theory (see Figure in left side for coronene). First principles and *ab initio* methods of PECs for both pyrene and coronene species feature a barrier of ~0.4 eV and a potential well of ~-0.5 eV. Spin-polarized SCC-DFTB (SDFTB) performs better regarding the well depth but the barrier height is too low with <0.1eV. We modified the C-H repulsive parameter function E^{rep} to adjust the SDFTB interaction energy to the G2MS PEC of coronene, and are now able to obtain perfect agreement between the resulting SDFTB with improved E^{rep}(C-H) (SDFTB*) and G2MS. Figure 1 illustrates the excellent agreement between improved SDFTB* and G2MS for the H-attack on the center C atom of coronene; an almost identical PEC was computed for pyrene as well.

Using SDFTB* we performed microcanonical MD simulations of chemical sputtering of individual hydrogen atoms and the basal plane of graphite (0001) with 160 carbon atoms in a nearly square planar unit cell. Following previous modified reactive empirical bond order (REBO) semiclassical molecular mechanics simulations, we probed a range between 0.1 and 100 eV for the H atom incident energy by supplying corresponding initial vertical velocities on the hydrogen atoms, which were placed in randomly chosen positions over the target graphite surface in up to 200 trajectories per incident energy. We recorded three kinds of interactions, adsorption, reflection, and penetration. Since SDFTB* features a much shallower adsorption well (~-0.5 eV) than the modified REBO potential (-4.8eV), the absorption yield and energy range is different (see Figure 2 for a comparison of reaction rates from REBO and SDFTB* MD simulations under identical conditions). In addition, SDFTB*/MD penetration occurs earlier compared to REBO, because the barrier height for hexagon penetration is only 5 eV as compared to 30 eV in the case of REBO. Our results indicate that lower graphite layers should be affected by lower hydrogen compared to the REBO MD simulations.

In summary, we have shown that improved SDFTB* can allow MD simulations for the chemical sputtering of H on graphite surfaces, and we are now working to perform similar simulations for multiple H adsorption and chemical sputtering on nanocrystalline graphite edges instead of basal plane attacks.

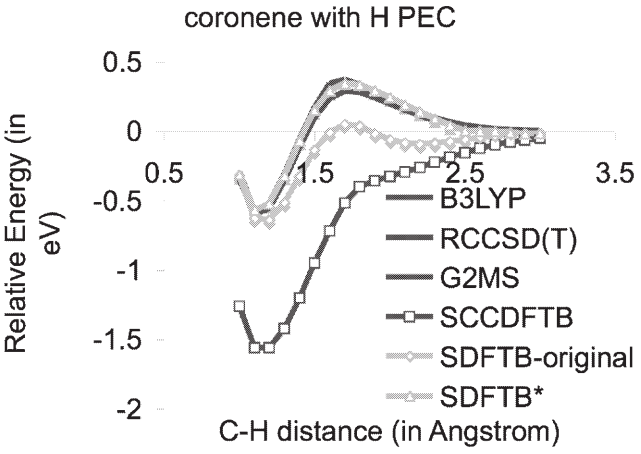

Fig. 1. Potential energy curve (PEC) for H-attack on center C atom of coronene; various quantum chemical methods including newly developed SDFTB* coinciding with high-level ab initio G2MS method.

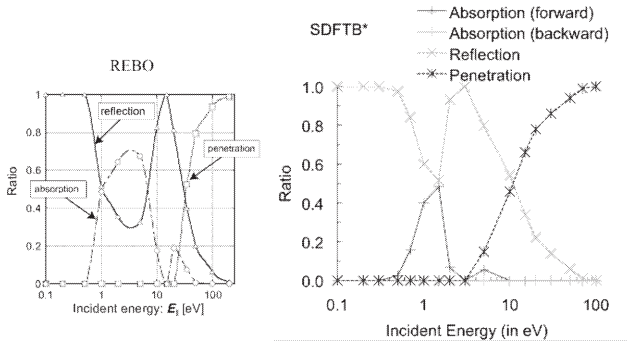

Fig. 2. Comparison of reaction rates for reflection, adsorption, and penetration of an H atom with incident energies ranging between 0.1 to 100 eV, using REBO and SDFTB* MD simulations for identical conditions as presented in Ref. [1)]

1) Nakamura, H.; Takayama, A.; Ito, A.; Contrib. Plasma Phys. **48** (2008) 265.