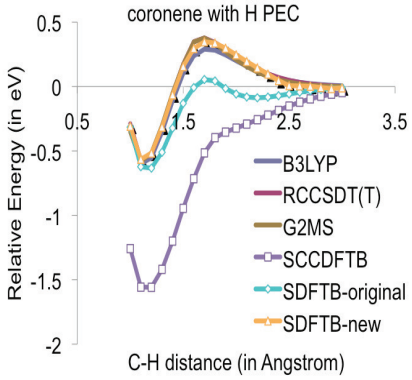
3E05

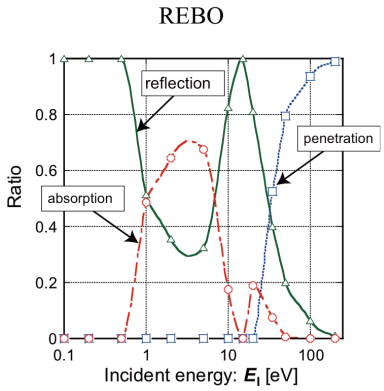
Chemisorption of Hydrogen on Graphite (0001): Spin-Polarized Density-Functional Tight-Binding Molecular Dynamics Simulations Using G2MS-Derived C-H Parameters

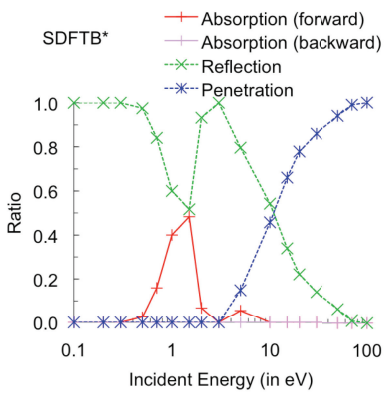
(IAR,Nagoya University[1], NIFS, Gifu[2], FUKUI, Kyoto University[3], Emory University[4]) ○Wang Ying[1], Ito Atsushi[2], Nakamura Hiroaki[2], Irle Stephan[1,2,3,4], Morokuma Keiji[1,2,3,4]



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.

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 than the modified REBO potential (-4.8eV), the absorption yield and energy range is different. In addition, SDFTB*/MD penetration occurs earlier compared to REBO. Our





results indicate that lower graphite layers should be affected by lower hydrogen compared to the REBO MD simulations.