

Density-Functional Tight-Binding Studies of Finite-Size Hexagonal Graphite Flakes

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Bond alternation patterns have been found in non-defective hexagonal graphene flakes (HGFs), according to theoretical calculations carried out at HF, DFT, MP2, and SCC-DFTB levels of theory for benchmark systems up the size of about 100 atoms, and on HGFs up to 1000 atoms using the SCC-DFTB method. It is convenient to provide an unambiguous notation system for these structures, beyond the chemical formula, and thus we characterize the HGFs with chirality indices (n,m) in analogy to single-walled carbon nanotubes. Here, the chiral indices denote the distance of one of the symmetry-equivalent six corner hexagons from the central hexagon. $(n,0)$ HGFs have zigzag-type borders, (n,n) flakes have armchair-type borders, and (n,m) flakes have chiral structure.

To visualize geometrical patterns in the series of HGFs characterized by bond differentiation breaking the bond equivalency of infinite-size graphite layers, we use graphical analysis of ring bond dispersion (RBD) and mean bond lengths (MBL), which are defined as in [1]:

$$RBD = \sqrt{\sum_{i=1}^6 (x_i - \bar{x})^2}; MBL = \bar{x} = \frac{1}{6} \sum_{i=1}^6 x_i$$

As in the case of finite-length SWCNTs [1], the bond differentiation patterns observed in finite-size (n,m) HGFs correspond to overall Clar and Kekulé schemes. Clar scheme presents an enhanced local aromaticity, while Kekulé scheme shows a higher electron localization into more double and single-character bonds. Depending on the particular border shape, the inner section for the graphene may or may not present bond differentiation. While for sheets having a zigzag border no differentiation is appreciated, for chiral and armchair border structures, neighboring bonds present a measurable difference, even in the center of the structure which is higher if the borders' indices are closer to those of an armchair border.

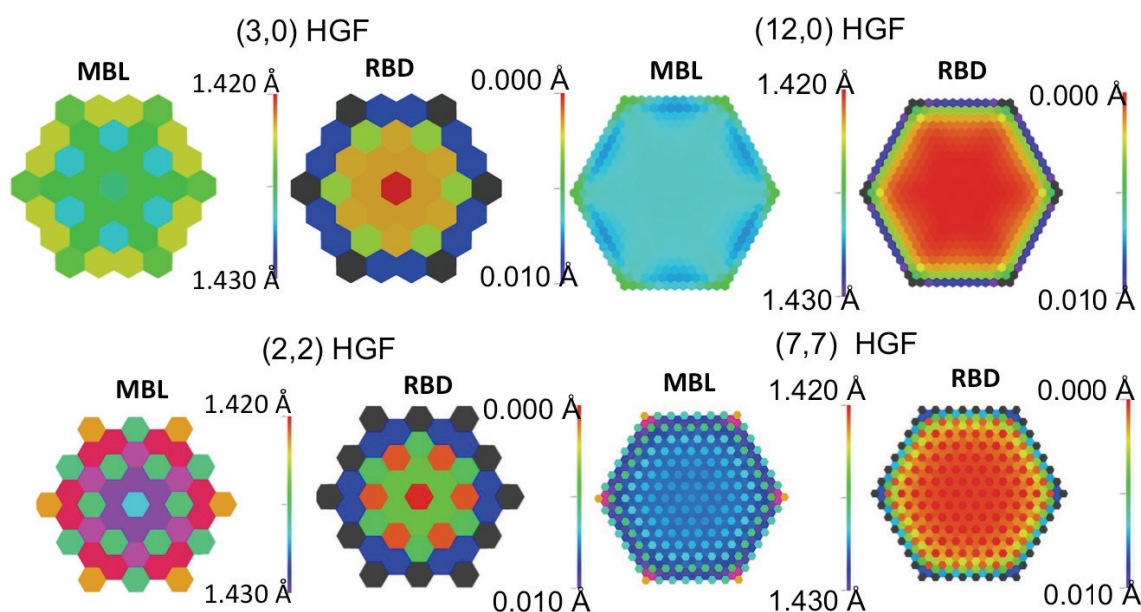


Figure 1: Mean bond lengths (MBL) and Ring bond dispersion (RBD) analysis of optimized HGFs structures by SCC-DFTB method (Te=0K)

Experimentally, graphene flakes can nowadays be characterized by Raman spectroscopy. As in SWCNTs, graphene flakes show strong Raman bands in the region around 1350 cm^{-1} (D-band) and 1590 cm^{-1} (G-band). Tuinstra *et al.* were first to attribute the origin of the D-band in disordered graphite (hence the notation “D”) to the change in selection rules in going from infinite graphite to microcrystalline graphite “big molecule” fragments [2]. They argued that the A_{1g} modes corresponding to individual hexagon breathing are visible only in finite graphite flakes, as their amplitudes do not exactly cancel out in this case. Necessarily, there exists a critical crystallite size L_a corresponding to a maximum of the $I(D)/I(G)$ intensity ratio, from where this ratio declines with $1/L_a$ behavior [3]. We have computed the Raman spectra of (1,0) to (13,0) HGFs using analytical second geometry derivatives for SCC-DFTB as implemented in [4], and demonstrate for the first time indeed the intensity of the G-band increases from $L_a \sim 46\text{ \AA}$ for (13,0), which corresponds to a $C_{1176}H_{84}$ molecule (see Figure 2). The origins for the intensity changes will be explained in the talk.

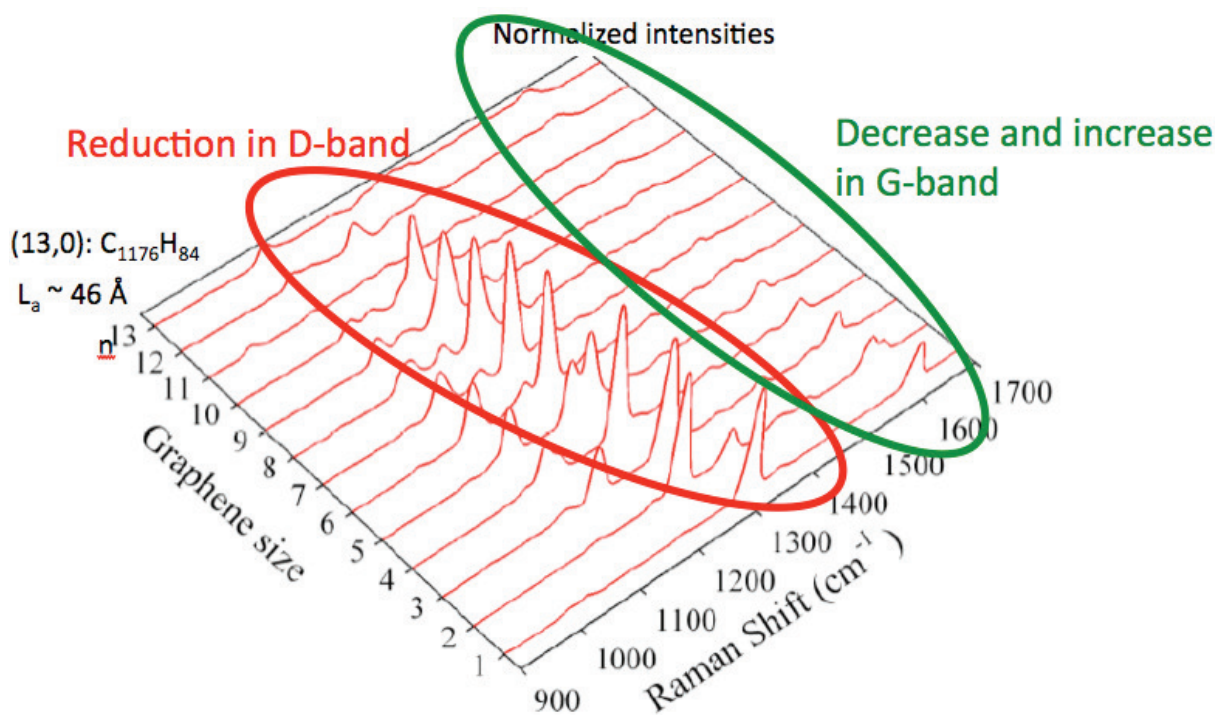


Figure 2. Change of Raman intensities of D- and G-band for (n,0) HGFs.

References

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