Nanostructured surfaces

Quantum-chemical calculation and visualization of the fundamental vibrational modes of graphene in different points of the Brillouin zone

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Quantum-mechanical calculations is very important in modern research of structure and physicochemical properties of molecules. Actual clusters allow calculations of the energy characteristics and vibrational spectra of polyatomic molecules. We used parallelized implemented software at GAUSSIAN09 packages [1] for calculations.

In this paper the conformational structure and vibrational spectra of single-layer and two-layer graphene were investigated using STO-3G basis and density functional theory (DFT) with the correlation functional VWN5 and periodic boundary conditions (PBC). As an initial atomic configuration fragment, an ideal flat hexagonal lattice of 40 carbon atoms (the distance between the atoms was 1.412 Å), or 12 elementary hexagonal cells of graphene with symmetry type D_{6h} was modeled and optimized in the same basis and functional.

Fundamental modes of graphene layer at Γ, K and M points of Brillouin zone were identified using the apparatus of the quantum mechanical projection operator. To optimize the search of the characteristic frequencies, the discrepancies between the experimental and calculated frequencies of the vibrational spectra were analyzed. Analysis of atom movements at graphene lattice for the main observed bands in the vibrational spectra was done. Thus, oscillations at 1689 cm^{-1} and 1705 cm^{-1} frequencies (non-coincidence is connected with not enough accuracy - 90%), which corresponds to a double degenerated state with the $(E_1^+)_\alpha$ and $(E_1^+)_\beta$ by Bir and Pikus classification [2] or E_{2g} by Dresselhaus notation at Γ-point of Brillouin zone that experimentally can be observed near 1600 cm^{-1} and called G-mode; oscillation at a frequency of 1455 cm^{-1} associated with the K-point Brillouin zone and observed at different frequencies of laser excitation at 1250-1380 cm^{-1} and called D-mode, the oscillation frequency at 1500 cm^{-1} associated with the i-TO phonon at M-point of Brillouin zone and appeared at unideal graphene and on the boundaries [3]. The discrepancy in the frequencies between experiment and calculation seems to be reduced by usage of SVP basis set.

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