

Ro-vibrational spectroscopy of molecular hydrogen confined to different carbon nanostructures

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Using density functional based symmetry adapted perturbation theory (DF-SAPT(DFT)), including its combination with dispersionless functional theory d1DF, we estimate the orientation-dependent interaction potentials of molecular hydrogen with carbon nanostructures, including graphite, graphene [1] and single-wall carbon nanotubes (both inside [2] and outside [3]). These potentials are further used to calculate quantum energy levels in the reduced confined space. We show that for graphene and graphite, the motion is effectively two-dimensional. The resulting energy levels for graphite compare very well with experiment (Fig. 1). We show that the hydrogen molecule behaves as a free rotor, with weak Stark effect caused by induced dipole interaction with a surface. The energy levels at graphite surface are compared to those of molecular hydrogen physisorbed at the metallic Cu(100) surface [4] where much stronger anisotropy was observed.

For carbon nanotubes, the motion is essentially three-dimensional (but the Hamiltonian depends on the overall rotation quantum number Λ). For positions both outside and inside wide nanotubes (e.g. with helicity (10,5)), it is again behaves as a perturbed free rotor, with the overall rotation of the whole molecule acting as a small perturbation. For external position, in a contrast to graphene surface, an energy splitting for the two parallel orientations (along and perpendicular to nanotube axis) is demonstrated, and explained by the different orientations of the associated induced dipole moments (Fig.2).

Instead, for narrow tube with helicity index of (5,5), the internal rotation is of similar amplitude as for an external one, so the energy levels are much more perturbed and less regular.

References:

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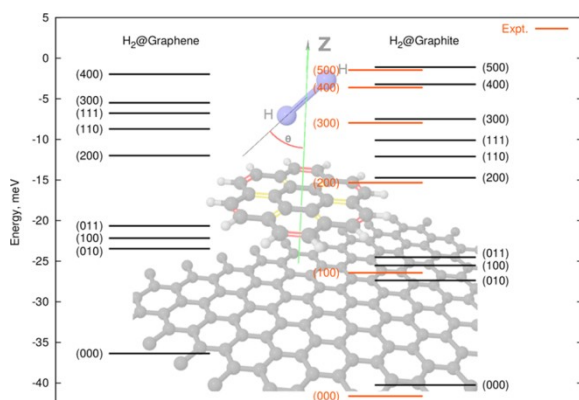


Fig.1 Energy levels for H₂ molecule on graphene and graphite surfaces

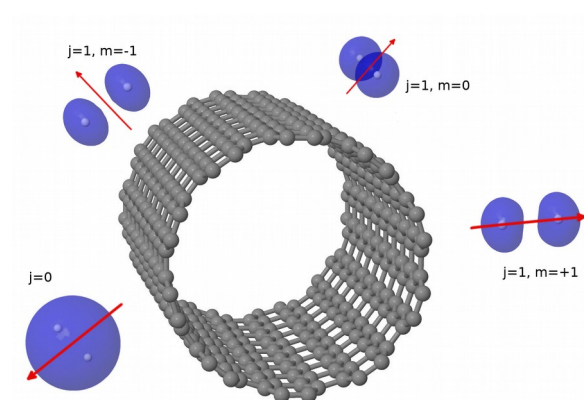


Fig.2 Illustration of energy m-splittings for H₂ on (10,5) SWCNT due to different orientation of molecule with respect to induces dipole moment