AB INITIO AND DFT STUDY OF COHESIVE ENERGY AND VIBRATIONAL SPECTRA OF FULLERENE DIMER, C_{120}.

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The methods of vibrational spectroscopy were shown to be a reliable and convenient tool for the characterization of C_{60} polymers resulted from (2+2)-cycloaddition of fullerene molecules. Though the IR and Raman spectra of 1D and 2D polymeric phases are well-understood empirically (1-2) their complete interpretation meets some computational difficulties in the employment of high-level theoretical approaches to the systems of such dimensionality.

On this way, the fullerene dimer is a key molecule to probe the different levels of the theory to describe adequately the energetics and vibrational spectra of inter-fullerene compounds. At the same time, despite the numerous calculations of C_{120} properties (3-7) even the sign of dimerization heat effect is up to now the matter of a discussion (Table 1).

We have fulfilled Hartree-Fock and DFT (in the GGA/PBE form) calculations of the geometry, energetics and vibrational spectra of C_{120} molecule employing the representative basis sets using both the PC GAMESS parallel version (8, 9) and DFT program package (10).

The cohesive energy of two C_{60} moieties in a molecule of C_{120} were calculated as the difference of C_{60} and C_{120} molecules total energies at HF/3-21G, HF/6-31G* and PBE/TZ levels in the course of the full geometry optimization as well as within the single-point energy calculations at the HF/6-311G* and PBE/QZ levels. The study verified an extremely low value of the energy and revealed its systematic decrease (or increase of «unbound energy») with the basis set widening. The result indicates thus the importance of the ZPVE and BSSE corrections for the theoretical value.

The vibrational spectra of C_{120} were simulated at the HF/6-31G* and PBE/TZ levels of the theory. The DFT results were found to match the experimental data (1) slightly better, especially in the region below 1000 cm^{-1}. Complete interpretation of the spectra was achieved within the scaling of the quantum-mechanical force field. Projecting technique was used to follow the parent cage vibrations in the complex modes of the dimer molecule.

Table 1. The enthalpy of C_{60} dimerization calculated at different levels of theory, kcal/mol.

Method/basis	ΔH	Ref.
PM3	-36.90	3
TB	6.23	3
DF-TB	-6.92	4
QMD	10.84	5
LDA/3-21G	-29.98	6
LDA//DF-TB	-27.67	4
BLYP/6-311G*//MNDO	17.30	7
BLYP/3-21G	8.20	7
PW92//DF-TB	-7.38	4
B3LYP/3-21G	5.07	6
B3LYP/6-31G*//3-21G	1.15	6
HF/3-21G	-10.29	6
This work		
HF/6-31G*	-1.40	
HF/6-311G*//6-31G*	0.17	
ΔZPVE	1.31	
PBE/tz2p	1.74	
PBE/qz//tz2p	4.41	
ΔZPVE	1.06	

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