APPLICATION OF DENSITY FUNCTIONAL THEORY TO ANALYSIS OF THE VIBRATIONAL SPECTRA OF pi-COMPLEXES OF TRANSITION METALS

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Functional density theory is applied to a study of vibrational spectra of naphthalene (C_10H_8), 1,4,5,8- and 2,3,6,7-tetradeuteronaphthalenes (α- and β-$C_10H_4D_4$) and (π-naphthalene)chromium tricarbonyle, (η^6-C_10H_8)Cr(CO)$_3$. Geometrical parameters, force fields, vibrational frequencies, and IR intensities were calculated for above molecules. A good correspondence of the calculated and experimental spectra was obtained without application of a scaling procedure for force constants. The full assignment of vibrational modes is carried out. The influence of metal-ligand π-bond formation on geometrical parameters and force fields of cyclic aromatic ligands is discussed. The data on force field changes are obtained for both the metal-bonded and non-bonded benzene rings of the naphthalene ligand . The structure of bis(cyclopentadienyl)zink molecule (Cp_2Zn) has been a subject of discussions for many years. The IR and Raman spectra of Cp2Zn in the solid state and in solutions were measured and discussed in connection with the structure of this compound. An unusual slip-sandwich molecular structure (η^5-C_5H_5)(η^1-C_5H_5)Zn in solution is proposed based on an analysis of the spectra in the regions of metal-ligand and out-of-plane ρ(CH) bending vibrations. DFT calculations of the Cp_2Zn structure with different basis sets confirm that the sandwich structure (η^5-C_5H_5)$_2$Zn (A) is not energetically advantageous, and more expedient are the π,σ-structure (η^5-C_5H_5)(η^1-C_5H_5)Zn (B) and σ-structure (η^1-C_5H_5)$_2$Zn (C). The energy difference between the B and C structures is insignificant (about 0,3 kcal/mol). The spectra of isolated molecules Cp_2Zn calculated with the DFT force fields coincide badly with the experimental data and do not allow us to choose between the B and C structures. In our opinion, it is connected with a structural non-rigidity of a Cp_2Zn molecule and with a strong dependence of its structure on the nearest surrounding in solution or the crystalline state.