

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 ($C_{10}H_8$), 1,4,5,8- and 2,3,6,7-tetradeuteronaphthalenes (α - and β - $C_{10}H_4D_4$) and (π -naphthalene)chromium tricarbonyl, (η^6 - $C_{10}H_8$)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)zinc molecule (Cp_2Zn) has been a subject of discussions for many years. The IR and Raman spectra of Cp_2Zn 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)₂Zn (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)₂Zn (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.