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

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Functional density theory is applied to a study of vibrational spectra of naphthalene (C\text{10}H\text{8}), 1,4,5,8- and 2,3,6,7-
tetra(deuterio)naphthalenes (\(\alpha\)- and \(\beta\)-C\text{10}H\text{4}D\text{4}) and (\(\pi\)-naphthalene)chromium tricarbonyl, (\(\eta^5\)-C\text{10}H\text{8})Cr(CO)\text{32}. 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 \(\pi\)-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\text{2}Zn) has been a subject of discussions for many years. The IR and Raman spectra of Cp\text{2}Zn 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 (\(\eta^5\)-C\text{5}H\text{5}\text{2})(\(\eta^1\)-C\text{5}H\text{5})Zn in solution is proposed based on an analysis of the spectra in the regions of metal-ligand and out-of-plane \(\rho\)(CH) bending vibrations. DFT calculations of the Cp\text{2}Zn structure with different basis sets confirm that the sandwich structure (\(\eta^5\)-C\text{5}H\text{5}\text{2})Zn (A) is not energetically advantageous, and more expedient are the \(\pi\)-\(\sigma\)-structure (\(\eta^1\)-C\text{5}H\text{5})(\(\eta^1\)-C\text{5}H\text{5})Zn (B) and \(\sigma\)-structure (\(\eta^1\)-C\text{5}H\text{5})\text{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\text{2}Zn 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\text{2}Zn molecule and with a strong dependence of its structure on the nearest surrounding in solution or the crystalline state.