A benchmark of DFT methods for the prediction of rotational and vibrational spectra of difluoromethane

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In a recent paper the vibrational spectrum of difluoromethane has been simulated by CCSD(T) theory in conjunction with basis sets of quadruple-zeta quality to an accuracy of 2.7 cm^{-1} [1]. Although coupled cluster theory and large basis sets are able to reach impressive accuracies, at present they are still calculations affordable only for small to medium sized molecules. Methods rooted in density functional theory represent a very promising answer for large molecules or systems composed of tenth to hundreds heavy atoms. For example, they appear the only practical choice in for the theoretical modeling of periodic structures, such as the study of adsorption processes on crystal surfaces.

In order to explore the reliability of DFT in rotational and vibrational spectroscopy, the performances of five popular DFT methods in predicting rotational and vibrational properties of molecules have been extensively studied, taking CH_2F_2 as a test case. This molecule has been selected not only because of the presence of very accurate CCSD(T) and experimental data, but also because the description of C-F bonds is very challenging due to the presence of electronegative fluorine atom. In particular, three hybrid- (B3LYP, PBE0, B3PW91), one GGA- (B97-1) and one double hybrid (B2PLYP) functionals have been considered by employing several basis sets (belonging to Pople, Dunning, Jensen, Ahlrichs, ANO or N07 families), of single up to sextuple zeta quality. Results concerning the predictions of geometries, rotational constants and vibrational transitions frequencies and intensities of CH_2F_2 are reported with respect to CCSD(T) calculations, taken as reference.

[1] N. Tasinato, G. Regini, P. Stoppa, A. Pietropolli Charmet, A. Gambi, J. Chem. Phys. **2012**, *136*, 214320.