On the performance of exchange-correlation functionals in the calculations of vibrational reorganization energy

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In last decade, the integrated computational approach going beyond vertical approximation has been developed and applied to the simulations of vibrationally-resolved absorption spectra of various medium- and large-sized organic chromophores [1]. Due to the fact that TD-DFT constitutes the most widely used approach in the modeling of excited states of this class of molecules, the choice of adequate exchange-correlation functional is of pivotal importance [2]. In current literature there is a number of benchmarks aiming to pinpoint the most suited computational protocol for the simulations of electronic absorption spectra [2,3], however none of these works has examined thoroughly the performance of TD-DFT in the computations of the vibrational reorganization energy (λ_v) which is directly related to absorption band shape.

Herein, we show that based on the values of vibrational reorganization energy for a given training set, one can pre-screen the performance of tested computational protocol without the need for direct comparison of the simulated spectra. In so doing, we examine the chosen exchange-correlation functionals, i.e. BLYP, B3LYP, BHandHLYP, CAM-B3LYP, LC-BLYP, LC-ωPBE, M06, M06-HF, M06-2X, PBE0, PBE, ωB97X, and ωB97XD in the calculations of λ_v for a set of pyridine-based difluoroborate compounds which have become recently of high interest owing to their outstanding photophysical properties [4]. The computations were carried out based on the linear coupling model in the gas phase. The outcomes were confronted with the reference values obtained at the CC2/cc-pVTZ level of theory and the experimental data.

Noteworthy, the analysis of results obtained by using tested functionals reveal substantial discrepancies in vibrational reorganization energy. In all cases M06-HF overshoots significantly the values of λ_v by yielding the relative error higher than 50 percent. On the other hand, the functionals M06-2X, ωB97XD and CAM-B3LYP are close to reference spot and lead to correct band shapes. Taken together, one should be particularly cautious while selecting the computational protocol to accurately reproduce the vibrationally-resolved spectra of difluoroborates. Nevertheless, the calculations of vibrational reorganization energy based on computationally efficient linear coupling model can help in selecting a subset of functionals for more detailed investigations.

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