Determining Optical Spectra with Theory: an Easy Challenge ?

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During this lecture, I will illustrate with several families of organic molecules, how it is possible, yet challenging, to model absorption and emission spectra with an approach that is both physically sound and reasonably accurate. Time-Dependent Density Functional Theory (TD-DFT) that has become the *de facto* standard theory in excited state simulation will indeed be used to model both 0-0 energies and vibronic contributions.[1]

The results of various TD-DFT benchmarks relying on several protocols and assessing a large set of exchange-correlation functionals will be briefly commented,[2] not only to pinpoint a limited number of optimal functionals, but also to provide estimates of the expected TD-DFT accuracy. Cyanine transitions, that are particularly challenging for TD-DFT,[3,4] will be treated in the framework of "real-life" applications, e.g., BODIPY dyes and their derivatives.[5,6] Eventually, the advantages of using theory to model Excited-State Intramolecular Proton Transfer (ESIPT) will be discussed.[7]

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