Modeling the Optical Spectra of the Indocarbocyanine Cy3 Using the Ensemble and Franck-Condon Approaches

Mohammed Sorour[1], Andrew H. Marcus[2], Spiridoula Matsika[1]

1 Department of Chemistry, Temple University School of Science and Technology (CST), Philadelphia, PA

2 Center for Optical, Molecular and Quantum Science, University of Oregon, Eugene, OR

The labelling of proteins and nucleic acids with fluorescent probes is a powerful approach to map out the site-specific structure of such systems. Accurate modeling of the chromophoric optical spectra is crucial for the correct inference of the molecular dynamics. The Marcus group conducted optical experiments on dsDNA internally labeled with Indocarbocyanine Cy3 monomers and dimers. In this work, the absorption spectrum of the Cy3 monomer is simulated using the ensemble approach via classical sampling and quantum sampling, as well as, the Franck-Condon approach. The factors limiting the ensemble approaches including the sampling and force field effects are tested, while the vertical and adiabatic harmonic approximations of the Franck-Condon approach are also systematically examined. Our results show that all the vertical methods, including the ensemble approach, are not suitable to model the absorption spectrum of Cy3, and recommend the adiabatic methods as suitable approaches for the modeling of spectra with strong vibronic contributions. We find that the thermal effects, the low frequency modes, and the simultaneous vibrational excitations have prominent contributions to the Cy3 spectrum.