

Benchmark calculations of absorption spectra for fluorescein and related dyes in various environments

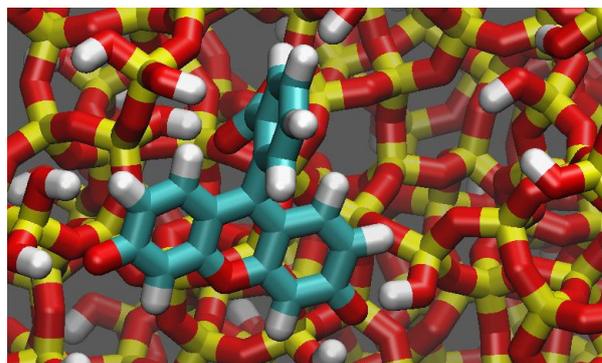
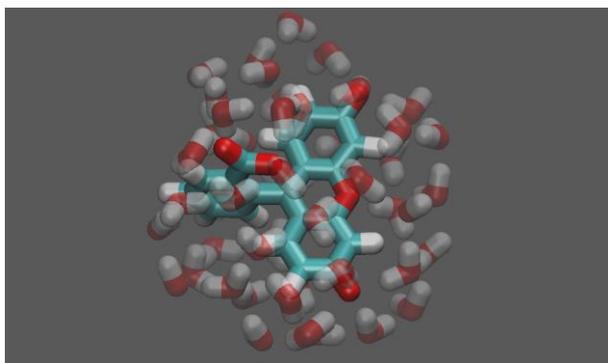
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Fluorescein adsorbed on an amorphous silica substrate is widely used in materials for optical chemical sensors in biology. Fluorescein and its chemical derivatives normally exist and fluoresce in anionic or even dianionic forms. Therefore, numerous calculations by different quantum-chemical methods were performed for these compounds to determine a reliable and computationally feasible approach providing reasonable agreement with experimental spectral data.

First, we calculated the absorption spectra of ionic forms of fluorescein, rhodamine 123, Alexa Fluor 488, Oregon Green, and carboxyfluorescein dyes by TDDFT (PBE0/6-31G(d,p)). The calculated energies for the first electronic transition differ from the positions of the first peak in the experimental absorption spectra by approximately the same value of 0.5 eV for all the compounds. Then, we performed TDDFT calculations for the mono- and dianionic forms of fluorescein, considered as a representative example, using all different density functionals available in the GAMESS program and various basis sets ranging from double-zeta of triple-zeta augmented with polarization and diffuse functions. However, the results were, in general, unsatisfactory. In order to check the effects of real environment, we also performed TDDFT (PBE0/6-31G(d,p)) calculations for fluorescein surrounded by some water molecules, including H₃O⁺ and Li⁺ counterions, and by polarized continuum medium using the PCM model. In these calculations we did also not observe significant effects of the environment on the calculated spectral parameters of the dye. The results obtained using the CIS approximation were even worse.



At the next step, we studied the absorption spectra of the mono- and dianionic forms of fluorescein by the CASSCF and CASSCF/MCQDPT methods and obtained an excellent agreement with experiment. Again, taking into account the environment effects of water within the PCM model did not affect the calculated spectra.

Finally, we constructed models of fluorescein adsorbed on an amorphous silica substrate by molecular dynamics (MD) simulations. The broadening of the absorption bands were calculated using TDDFT calculations for 200 points in the calculated MD trajectories and compared the results with similar calculations for the isolated dye.

We conclude that the band positions and shapes for the absorption spectra of fluorescein and similar dyes adsorbed on an amorphous silica matrix are best described by a combination of CASSCF + MD/TDDFT methods.