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Experimental and Quantum Chemistry Investigations of Nitrazine Yellow Absorption Spectra on Organosilica Surfaces

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Research object: Nitrazine Yellow (3-[(2,4-dinitrophenyl)azo]-4-hydroxy-disodium salt, **NY**

Research rationale and objectives: The ability of NY to change color in solution is due to the presence of azo- hydrazone tautomerism and deprotonation of the system in an alkaline environment.
Characterization of molecular shapes and understanding of the mechanism of tautomerism is crucial for controlling the properties of the molecule depending on the polarity and acidity of the environment.

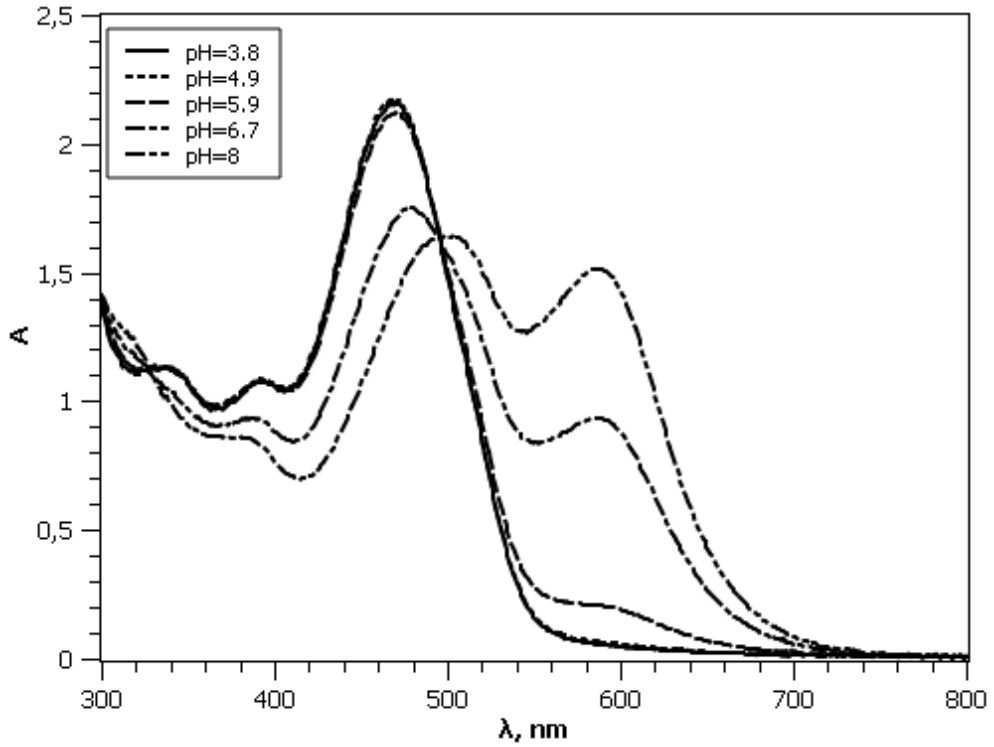
The aim of the work:

1) DFT calculations of geometry and electronic structures in the ground state and electronic absorption spectra in aqueous solutions and on silicon surfaces.

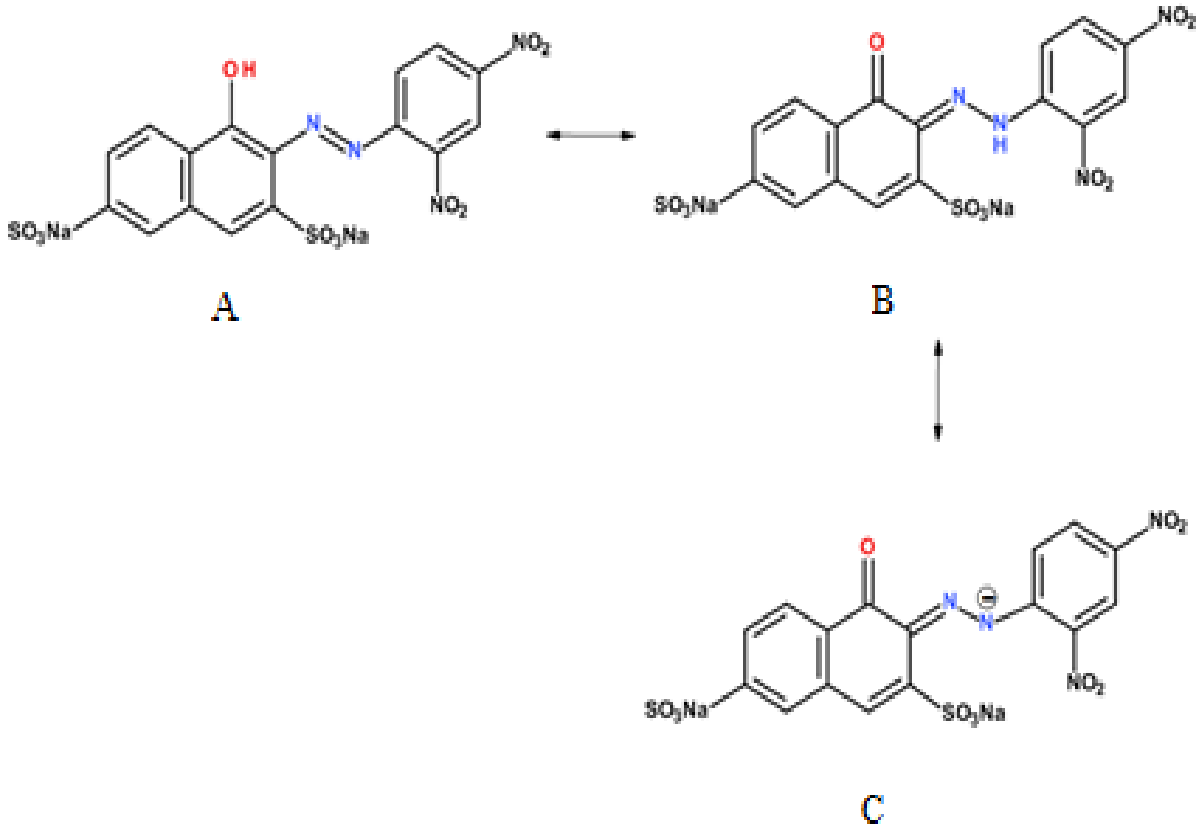
2) To compare results obtained with different DFT functionals and basis sets.

3)To compare theoretical results with experimental data.

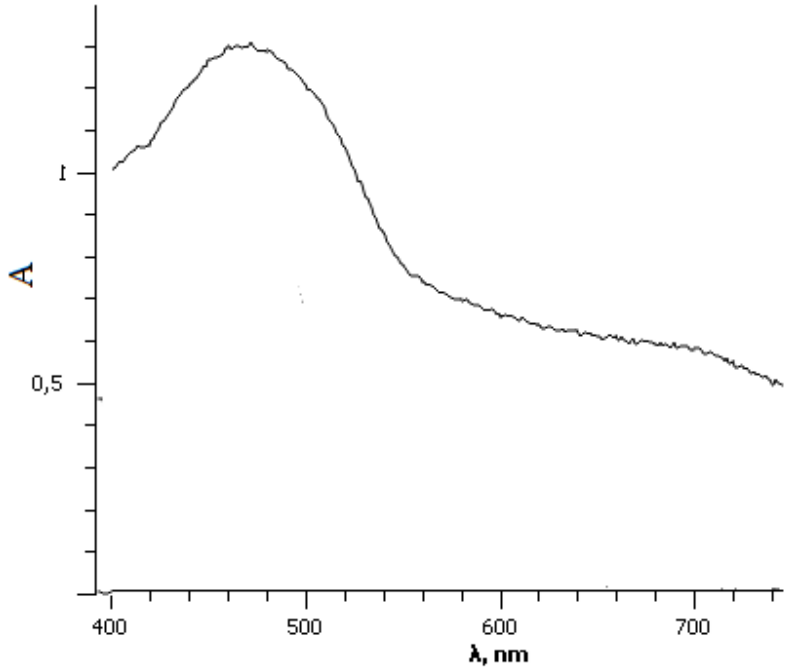
Three forms of NY in aqueous solutions

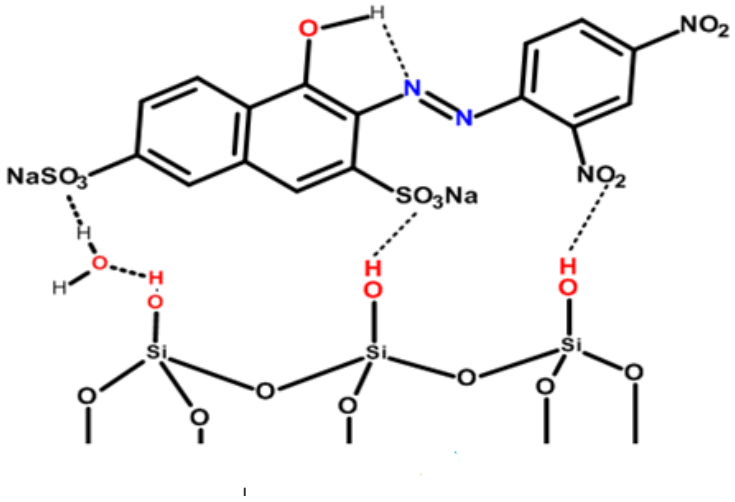


Absorption spectrum of an aqueous solution of NY at different pH values

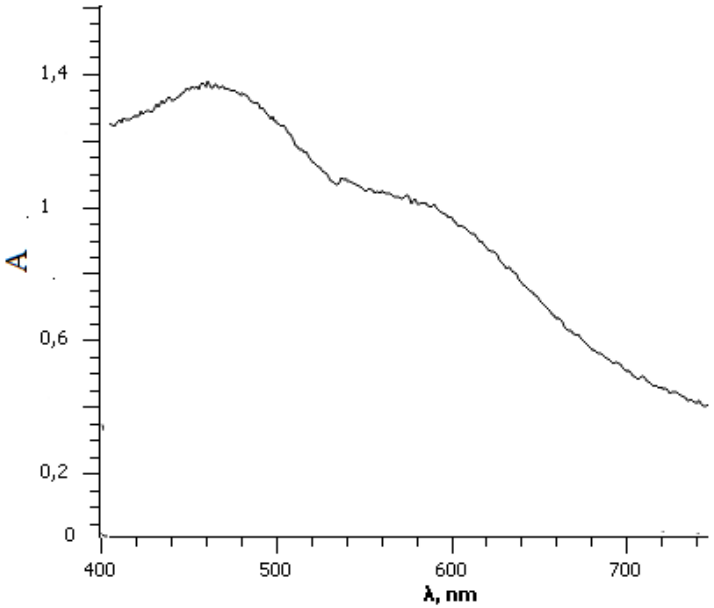


NY on silica surface



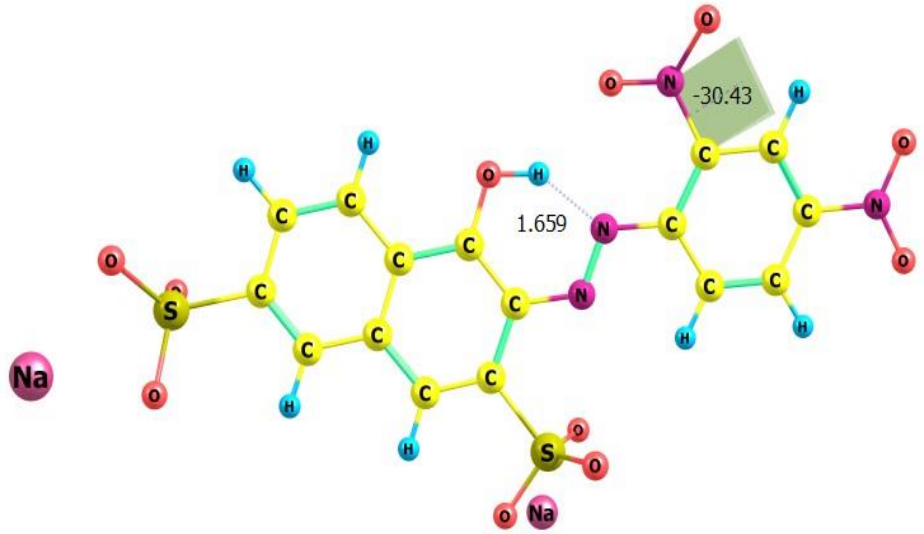


Absorption spectra of NY adsorbed on the surface of amino silica

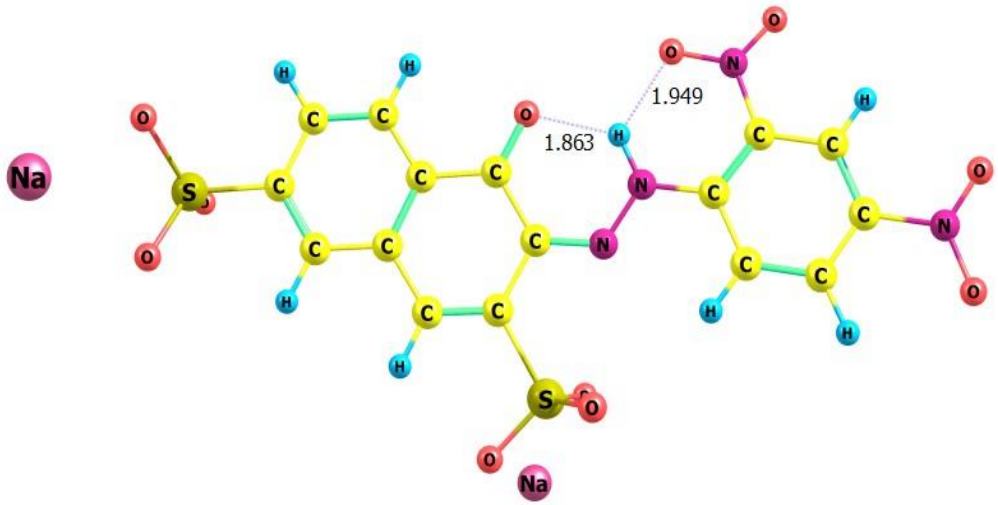


Absorption spectra of NY adsorbed on the surface of silica modified by N-(1-methyl-1-phosphonatoethyl) aminopropyl

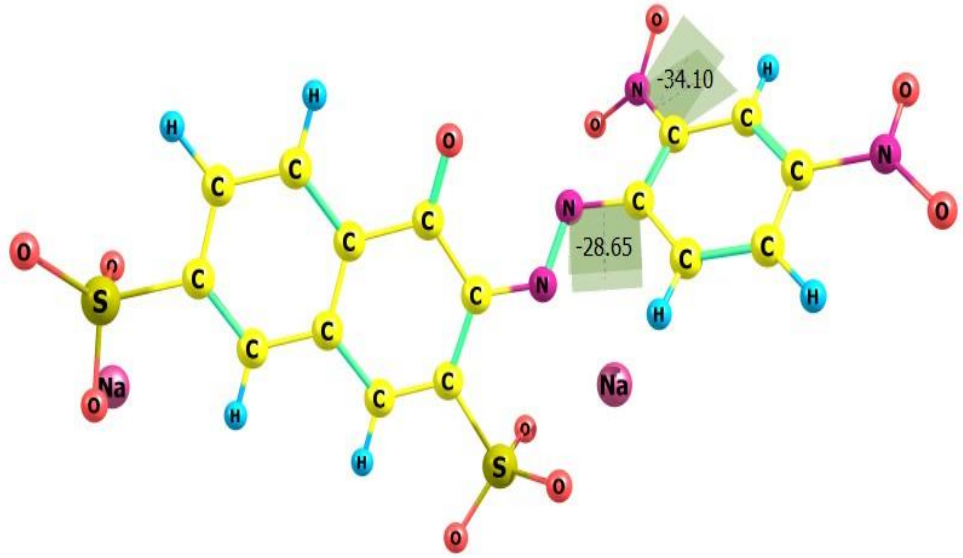
Three forms of NY. Ground state geometry B3LYP/6-31+G(d,p)



A

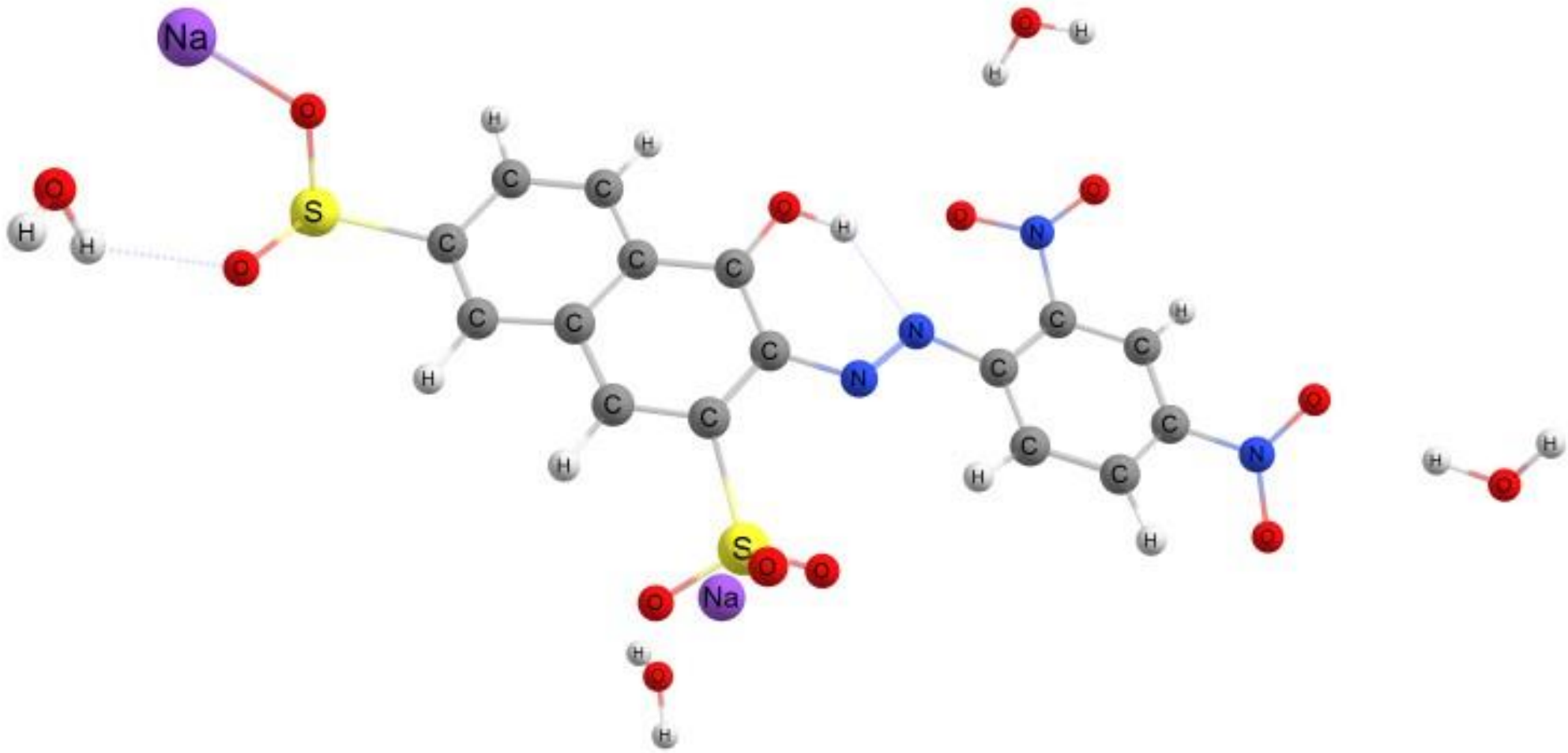


B



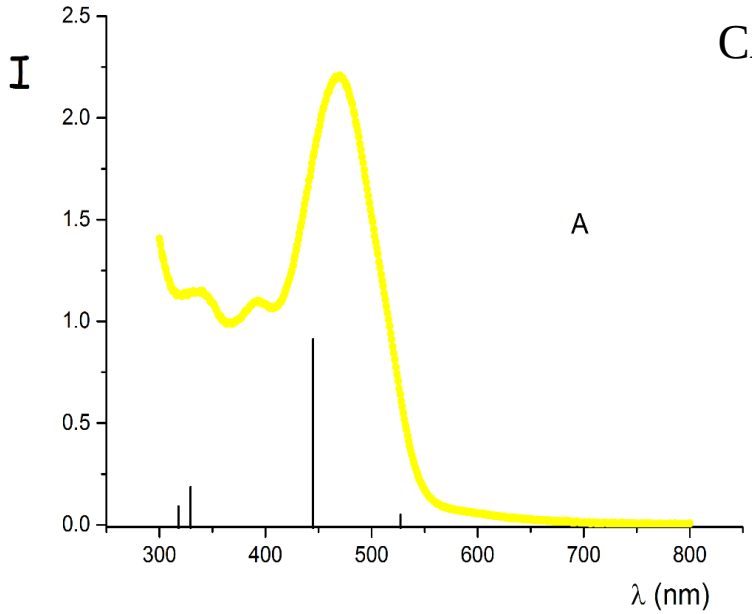
C

NY in aqueous solutions according to DFTB+ modeling

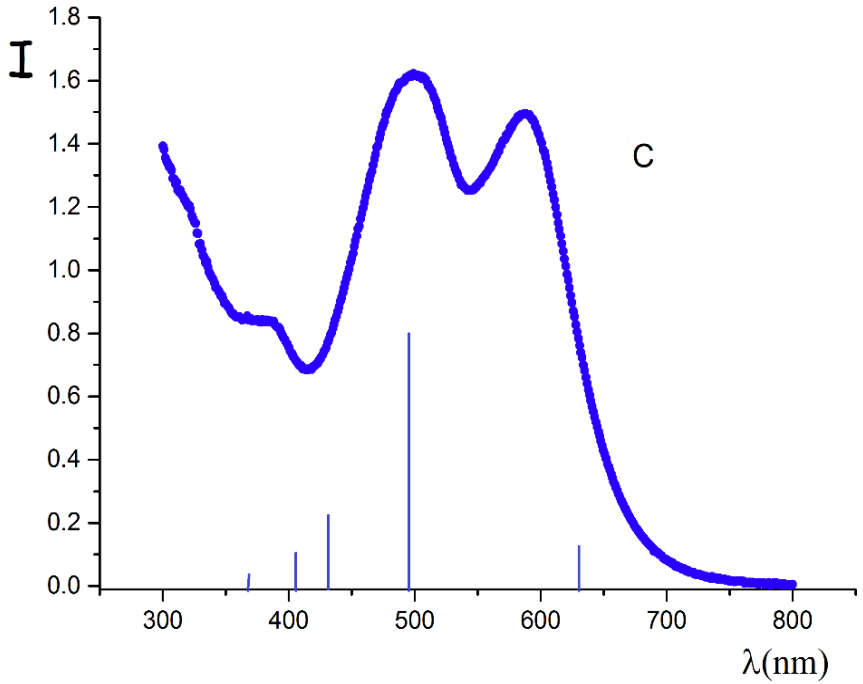


Correspondence between the experimental absorption band and calculated values of absorption wavelengths

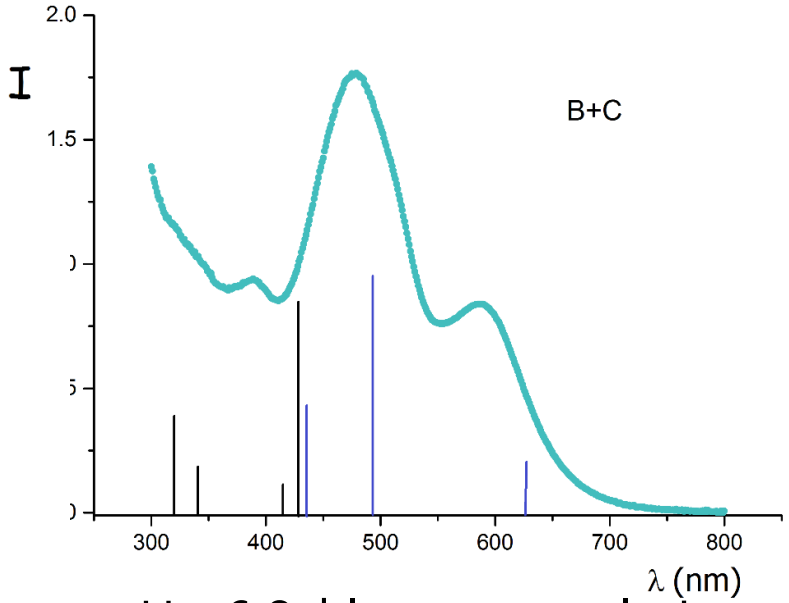
CAM-B3LYP / LanL2DZ / 6-31+G(d,p)



pH = 4.3, yellow solution



pH = 9.2, blue



pH = 6.8, blue-green solution

Conclusion

1) The B3LYP method gives significantly overestimated values of absorption wavelengths in all forms of the NY dye.
2) CAM-B3LYP slightly underestimates the absorption wavelength relative to B3LYP and to experimental data.
3) A pronounced batochromic shift was obtained in both the B3LYP and CAM-B3LYP functionals when switching from vacuum to solvent (water).
4) At pH ~ 6.8, the contributions of both the tautomeric form B and the deprotonated form C should be expected in the absorption spectrum.
5) The use of pseudo-potential methods (LanL2DZ) significantly reduces the calculations costs, although the agreement with the experimental data remains good.
6) Two variants of the CAM-B3LYP/LanL2DZ and the CAM-B3LYP/LanL2DZ/6-31+G(d,p) can be chosen for further use.