

# ELECTRONIC SPECTRA OF $\pi$ -STACKED PYRIMIDINE DIMERS: AN AB INITIO STUDY

**Maksimov D.A., Ramazanov R.R., Kononov A.I.**

Faculty of Physics, Saint Petersburg State University  
Ulyanovskaya 1, 198504, Saint Petersburg, Russia  
E-mail: da.maksimov.da@gmail.com

Excited states in multichromophoric systems have recently gained a substantial amount of interest. The interaction of DNA and RNA with ultraviolet (UV) sunlight in region above 290 nm is considered to be responsible for much photochemical damage, which leads to mutations, premature aging of the skin, and carcinogenesis. Structural deviations from the canonical B-form leads to significant change of the electronic states and the electronic excitation spectra. Absorption spectrum of some distorted structures can be slightly overlapped with terrestrial solar radiation in the region above 300 nm, where absorption spectra of nucleic acids falls dramatically, which makes such non-canonical structures a good targets for UV. Due to complexity of DNA and influences of the DNA backbone, even accurate spectroscopic measurements cannot provide detailed and precise information about the origin of the absorption, thus theoretical investigations play key role in understanding of the nature of photobiology processes.

To predict the absorption spectra of the  $\pi$ -stacked nucleobase dimers and monomers we calculated their vertical excitation energies and oscillator strengths. Energies of the excited states were calculated at configuration interactions singles (CIS) with double corrections level of theory and oscillator strengths were obtained from CIS computations using ORCA program. In order to obtain interatomic distances of methylled monomers in ground state geometry optimization with Hartree-Fock + Møller-Plesset perturbation theory of second order method which is implemented in GAMESS US package was used. We performed a detailed benchmark on excited energies positions depends on initial structure of monomers, using diffuse functions in basis sets and presence of solvent. Chemcraft was used to construct attachment and detachment of the electronic densities between ground and excited states in order to show the nature of the excitation transitions. Non-canonical forms of pyrimidine dimers were found in structures of nucleic acids in RCSB Protein Data Bank with use of MDAnalysis Python toolkit. All graphs were constructed with matplotlib package.

The low-energy transitions in all the studied structures exhibit the mostly pure exciton nature. Excitation appears to be delocalized over two bases, although a slight contribution of charge transfer between the bases to the overall state is possible. Interesting thing is that in some cases we observed rather large values of exciton splitting of monomer  $\pi\pi^*$  states that come to about 0.5 eV. This value greatly exceeds the usual values 0.1 - 0.2 eV calculated for canonical B-form of homodimers thus non-canonical forms of nucleic acid dimers can absorb light in region above 300 nm. Investigation of the distorted base-stacking conformations can probably help to understand the nature of cyclobutane pyrimidine dimers formation process, which leads to cancer diseases.