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Influence of the phytyl chain of chlorophyll *a* anionic on UV-vis spectra

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Plants contain chlorophyll-type molecules, which play a vital role in photosynthesis for several reasons. Photosynthesis, a well-known process, involves two distinct photosystems: Photosystem I (PSI) and Photosystem II (PSII). PSII serves as a catalyst and initiates the photosynthetic process. The negative charge is localized on a single chlorophyll molecule instead of two, as observed in the PSI dimer. To investigate electron transfer in PSII, it is imperative to understand the behavior of the chlorophyll *a* itself in gas phase.

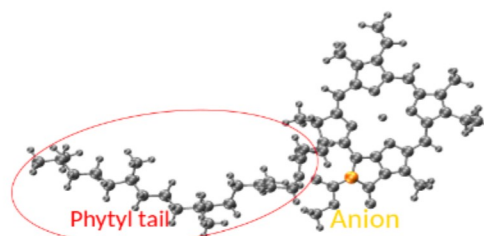


Figure 1: Chlorophyll *a* negative

This study aims to understand the effect of the phytyl chain on the UV-vis spectra of the chlorophyll *a* anionic in gas phase. Indeed, chlorophyll type molecule have a hydrocarbonated tail which is very flexible and moves a lot during dynamic, specially in gas phase. Based on a previous work, we used the molecule deprotonned on the macrocycle [1] presented on figure 1.

To answer this question, we built a step-by-step protocol. We carried out the Parallel Tempering molecular dynamic at the SCC DFTB method in deMonNano [2]. The exchange of configurations during parallel dynamics at various temperatures is a powerful tool for exploring the configuration space.

To understand how the phytyl chain moves, we deployed a clustering method called Hierarchical Density-Based Spatial Clustering of Applications with Noise (HDBSCAN) [3], [4]. This method belongs to the machine learning field and is applied on different kind of databases, it is used to group points of a database together called as cluster. In this idea, we built a database with representative measurements to characterize the phytyl chain in the space, using an angle and a distance between the macrocycle and the chain and a dihedral angle at the basis of the chain. We obtained different clusters representative of various configuration of the phytyl chain position in space.

To obtain UV-spectra specific for each configuration type, we have run TD-ADFT calculations with deMon2k [5]. We consider as reference chlorophyll *c2* which is the chlorophyll *a* without the phytyl chain and with an alcohol instead. Throughout this project, we employed a combination of methods, machine learning tool and SCC DFTB parallel tempering. We applied these methods to investigate the observation and characterization of phytyl chain conformations and their impacts on absorption spectra.

Keywords: Parallel tempering, DFTB, TD-DFT, UV-vis.

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