



HAL
open science

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

Julia Attard, Aurélien de la Lande, Philippe Carbonnière, Benois Soep,
Niloufar Shafizadeh

► **To cite this version:**

Julia Attard, Aurélien de la Lande, Philippe Carbonnière, Benois Soep, Niloufar Shafizadeh. Influence of the phytyl chain of chlorophyll a anionic on UV-vis spectra. XVIIIèmes rencontres ThéMoSiA-RCTF, Université de Rouen; INSA Rouen, Jun 2024, Rouen, France. hal-04793261

HAL Id: hal-04793261

<https://univ-pau.hal.science/hal-04793261v1>

Submitted on 20 Nov 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

ATTARD Julia,^{A,B} de la LANDE Aurélien,^A CARBONNIERE Philippe^B SOEP Benoît^C, SHAFIZADEH Niloufar^C

A) Université Paris Saclay, Institut de Chimie Physique, Orsay, France ; B) Université de Pau et des Pays de l'Adour, Institut des sciences analytiques et de physico-chimie pour l'environnement et les matériaux (IPREM), Pau, France ; C) Université Paris Saclay, Institut des Sciences Moléculaires d'Orsay (ISMO), France

julia.attard@universite-paris-saclay.fr

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.

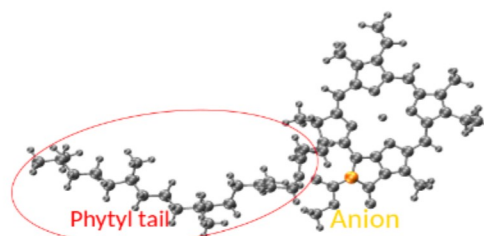


Figure 1: Chlorophyll *a* negative

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.

References

- [1] M. Diop, M. El-Hayek, J. Attard, A. Muhieddine, V. Veremeienko, S. Soorkia, Ph. Carbonnière, A. de la Lande, B. Soep, and N. Shafizadeh. Chlorophyll and pheophytin protonated and deprotonated ions: Observation and theory. *The Journal of Chemical Physics*, 159(19):194308, 11 2023.
- [2] Luiz Fernando L Oliveira, Jérôme Cuny, Maxime Morinière, Léo Dontot, Aude Simon, Fernand Spiegelman, and Mathias Rapacioli. Phase changes of the water hexamer and octamer in the gas phase and adsorbed on polycyclic aromatic hydrocarbons. *Physical Chemistry Chemical Physics*, 17(26):17079–17089, 2015.
- [3] Leland McInnes, John Healy, Steve Astels, et al. hdbscan: Hierarchical density based clustering. *J. Open Source Softw.*, 2(11):205, 2017.
- [4] Ricardo JGB Campello, Davoud Moulavi, and Jörg Sander. Density-based clustering based on hierarchical density estimates. In *Pacific-Asia conference on knowledge discovery and data mining*, pages 160–172. Springer, 2013.
- [5] Gerald Geudtner, Patrizia Calaminici, Javier Carmona-Espíndola, Jorge Martín del Campo, Víctor Daniel Domínguez-Soria, Robert Flores Moreno, Gabriel Ulises Gamboa, Annick Goursot, Andreas M. Köster, José Ulises Reveles, Tzonka Mineva, José Manuel Vásquez-Pérez, Alberto Vela, Bernardo Zúñiga-Gutierrez, and Dennis R. Salahub. demon2k. *Wiley interdisciplinary reviews. Computational molecular science*, 2(4):548–555, 2012.