

# Spectral Properties of the Phycocyanobilin Chromophore

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## 1 Abstract

Chromophores as the central, light absorbing part of the photoreceptors in plants and certain bacteria play a crucial role in the detection of light and triggering responses. The chromophore phycocyanobilin (PCB) is an open tetrapyrrole, that can be found in bacterial, plant and fungal phytochromes.

Recently, NMR experiments on the sole chromophore without the protein environment have been performed. Here, a full assignment of the carbon and nitrogen NMR chemical shifts for phycocyanobilin in the aprotic solvent HMPT has been achieved by triple resonance experiments. New experiments in methanol show different chemical shifts, which are unexplained so far. Within the framework of this HLRN project, we plan to unravel the molecular origin of these experimental findings by employing molecular dynamics simulations and theoretical NMR spectroscopy on the pycocyanobilin.

Our molecular dynamics simulations show a rich potential energy surface, with many local minima. We will explore this potential energy surface and discover all local minima. Our methods are based on a quantum mechanical description which allows us a highly accurate local sampling of all relevant regions of the phase space. We will exploit our first principles trajectories to perform theoretical NMR spectroscopy, which enables us to link our results to the experimental data. A particularly important aspect of our project is the inclusion of the direct interaction of the phycocyanobilin with a surrounding explicit solvent. Specifically we will perform calculations on a DFT/classical hybrid approach (QM/MM) which is the best known method for the inclusion of solvent hydrogen-bonding patterns. Our ab-initio calculations will allow us to gain insight into the very basic mechanisms of the chromophore solvent interaction, which is highly important for the full understanding of the chromophores function during the photocycle.