Using coherence signals to expose vibronic mixing in chlorophylls

Ignacio Martínez Casasús[1], Eglė Bukartė[1], David Paleček[1], Claudia Büchel[2], Donatas Zigmantas[1,*]

[1]*Chemical Physics, Lund University, Lund, Sweden*
[2]*Institute of Molecular Biosciences, Goethe University Frankfurt, Germany*
**donatas.zigmantas@chemphys.lu.se*

Electronic-vibrational (vibronic) coupling has been paroposed to play an important role in photosynthetic processes, such as energy transfer and charge separation. Even though this coupling in molecules has been suggested almost a hundred years ago, it has proven to be a highly elusive phenomenon to investigate. It can, however, be revealed by studying coherence signals. To this end we employ polarization-controlled 2D electronic spectroscopy together with advanced analysis that allows to extract full information about coherences, including their origin, which in turn directly reports on vibronic mixing of states.

In 2013 Raimers and co-workers proposed that vibronic mixing is ubiquitous in chlorophyll family of molecules[1]. We sought for the direct experimental confirmation and refinement of these ideas by studying two chlorophyll molecules. We started with a low temperature studys of Chl *c1*[2] and then carried out a following study on Chl a. By analysing coherences observed in 2DES experiments (Figure 1) we found clear evidence of vibronic mixing of the two lowest electronic states, Q_Y and Q_X. Importantly, we distinguished multiple vibrational modes that are involved in vibronic mixing.

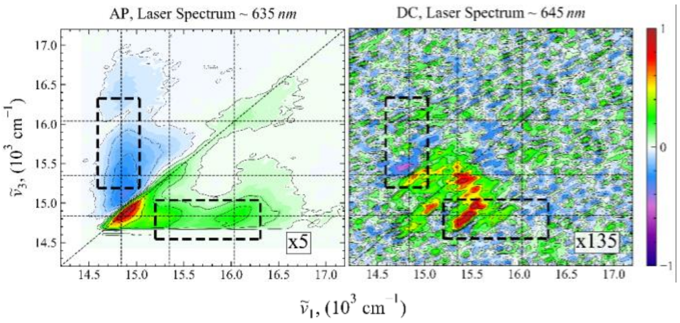

Figure 1: Absorbtive 2D spectra of Chl *a* at population time t_2=100 fs measured with all-parrallel (AP) and double-crossed (DC) pulse polarizations.

Results obtained in our studies together with numerous less direct indications of vibronic mixing in a large range of chlorophyllides clearly establish that vibronic mixing is ubiquitous and should be taken into consideration when studying various functions chlorophyllides perform in biological systems.

In principle vibronic mixing allows for subtly adjusting molecular quantum states to match resonances important for energy and electron transfer functions. Presence of the ubiquitous vibronic mixing in chlorophyllides and also in excitonic photosynthetic systems rises an intriguing question, if it is an unavoidable consequence of the properties of the porphyrin-type molecules, or an optimization mechanism, which nature employs to finely tune primary processes of photosynthesis.

References

1 J. R. Reimers, Z.-L. Cai, R. Kobayashi, M. Rätsep, A. Freiberg and E. Krausz, *Sci Rep*, 2013, **3**, 2761.
2 E. Bukartė, A. Haufe, D. Paleček, C. Büchel and D. Zigmantas, *Chemical Physics*, 2020, **530**, 110643.