

Vibrational-excitonic coupling in natural and artificial light harvesters

Jürgen Hauer¹

¹Photonics Institute, TU Wien, Gusshausstr. 27, 1040 Vienna, Austria, juergen.hauer@tuwien.ac.at

Coupling between vibrational and excitonic or electronic degrees of freedom has been at the center of an ongoing debate in the light harvesting community, and its functional relevance remains a controversial topic. [1] I will summarize the debate and give two examples where such vibronic coupling has been measured and analyzed, namely in an artificial [2] and a natural light harvesting complex. [3] In the latter case, vibronic coupling between the light harvesting pigments can be shown to have functional relevance, as it accelerates the transfer rate between carotenoids and bacteriochlorophylls.

Artificial light harvesters: Cyanine dyes arrange in closely packed cylindrical J-aggregates with nanometer-diameter and micrometer-length. Their efficient energy transfer pathways make them suitable candidates for artificial light harvesting systems. We use two-dimensional electronic spectroscopy with polarization-controlled excitation pulses to highlight purely excitonic pathways. In the double-walled cyanine dye aggregate (C8O3) [2] we use in our investigation, only pathways involving the inner tube, shielded from solvent-interaction, show long-lived coherences with lifetimes of up to 1.2 ps. We also find that the non-rephasing diagonal pathways show twice the oscillatory amplitude of rephasing off-diagonal signals. We describe both this finding and the detailed nature of the observed frequency evolution by a model allowing for vibronic coupling. The observed lifetimes are ascribed to lifetime-borrowing effects between vibrational and iso-energetic excitonic degrees of freedom. Our model, which accounts for specific cyanine-dye vibrations, also explains why vibrational signatures survive the polarization scheme specific to excitonic coherences. [4] We show that in our case of a macroscopically oriented sample with polarization-controlled excitation, the rephasing off-diagonal pathways proceed via ground state coherences; non-rephasing pathways on the other hand can only be explained by coherences in the excited state and are dominated by coupling between vibrational and excitonic degrees of freedom.

Natural light harvesters: While there is great structural diversity in bacterial light harvesting complexes, essentially only two molecular species serve as pigments, namely carotenoids and bacteriochlorophylls (red, BChls). After photo-excitation of a carotenoid, population is transferred to BChl. This initial transfer step is happening on the truly ultrafast timescale of 40 to 160 fs, depending on the organism in question. Such rapid transfer is a challenge for Förster theory, tending to overestimate the electronic coupling constant J . [3] We show that such high values of J cannot be reconciled with the shape of electronic 2D spectra or even linear absorption spectra of the investigated light harvesting complex, namely LH2 of *Marichromatium purpuratum*. We propose a vibronic coupling model, inspired by our work on artificial light harvesters mentioned above. In this model, the fast carotenoid vibrational modes couple strongly to the optical transitions and are part of the system's Hamiltonian. The retrieved transfer times depend on J as well as on the energetic detuning between donor and acceptor. The latter is determined by the absorption spectrum, while J is derived from structure-based calculations. We further validate the proposed vibronic coupling mechanism by testing it on an artificial carotenoid-purpurin dyad, where donor (carotenoid) and acceptor (a purpurin made to mimic the spectral properties of BChl) are covalently linked. The key ingredient to the mechanism, which dramatically speeds up energy transfer, is the deposition of excess excitation energy into the ground state vibrations of the carotenoid (donor) molecule.

In summary, vibronic coupling is established as the physical origin of long-lived oscillatory signals in 2D electronic spectra of light harvesting systems. Furthermore, the functional relevance of vibronic coupling is demonstrated by showing its influence on key parameters such as transfer times between energy donor and acceptors.

References

- [1] Huelga, S. F. Plenio, M. B. *Contemp. Phys.* **54**, 181 (2013).
- [2] J. Lim, J. Palecek, D. Caycedo-Soler, F. Lincoln, C. N. Prior, J. von Berlepsch, H. Huelga, S. F. Plenio, M. B. Zigmantas, D. Hauer, J. *Nature Comm.* **6** 7755 (2015).
- [3] Perlík, V. Seibt, J. Cranston, L. J. Cogdell, R. J. Lincoln, C. N. Savolainen, J. Šanda, F. Mančal, T. Hauer, J. *J. Chem. Phys.* **142** 212434 (2015).
- [4] Tiwari, V. Peters, W. K. Jonas, D. M. *Proc. Nat. Ac. Sci.* **110** 1203 (2013).
- [5] Blankenship, R. E. *Molecular Mechanisms of Photosynthesis* Wiley-Blackwell, Oxford, UK (2014)