Photosynthesis Exploits Quantum Coherence for Efficient Solar Energy Conversion

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Photosynthesis has found an ultrafast and highly efficient way of converting the energy of the sun into electrochemical energy: the Photosystem II Reaction Center (PSII RC) converts the energy into a charge separated state [1] with near unity quantum efficiency. That separation of charges creates an electrochemical gradient across the photosynthetic membrane which ultimately powers the photosynthetic organism. The understanding of the molecular mechanisms leading to charge separation will provide a template for the design of efficient artificial solar energy conversion systems.

In this work we have applied two-dimensional electronic spectroscopy on the fully functional PSII RC from higher plants at cryogenic and room temperature as well as standard Redfield modelling in order to investigate the presence and the role of quantum coherence in determining the high speed and efficiency of the charge separation process.

On the one hand, the experimental results show clear long-lived quantum beats in the 2D spectral traces at both temperatures. The set of frequencies contained in the beats (retrieved by Fourier transform) corresponds to intra-molecular Chl *a* vibrational modes and, interestingly, these frequencies match the difference in energy levels between the electronic states in the system. The 2D frequency maps (frequency amplitude distribution in the 2D spectra) strongly indicate that we observe vibronic coherence between the electronic states in the system, i.e., the long-lived electronic coherences are sustained by non-equilibrium vibrational modes [2]. On the other hand, the calculated 2D spectra by standard Redfield modelling using our current *disordered exciton-charge-transfer* model [3] are in excellent agreement with the experimental 2D spectra. This model also shows that the presence of electronic coherence between excitons and between excitons and charge-transfer states enhances the speed and efficiency of energy and electron transfer, respectively.

In conclusion, the combination of experimental and theoretical evidence strongly indicates that the PSII RC performs charge separation via a quantum coherent mechanism and, therefore, it operates as a *quantum designed light trap*. We propose that this design principle will inspire the development of new energy technologies.

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