

Vibronic Coupling as a Design Principle to Optimize Photosynthetic Energy Transfer

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SUMMARY

In this issue of *Chem*, Dean *et al.* report on observations of vibronic enhancement to energy transfer in the algal light-harvesting complex PC645 using two-dimensional electronic spectroscopy.

BODY

Photosynthetic organisms harvest energy from the sun using specialized nanometric antennae in which precisely arranged chromophores are bound to a protein scaffold. These molecular complexes absorb photons to form collective electronic excitations called excitons. Subsequent energy transfer steps within and between antennae, lead to conversion of energy in reaction centres. For several decades natural light-harvesting antennae have been the subject of intense research that aims to understand the microscopic mechanisms underlying their efficient performance when it comes to concentrate and transfer excitation energy¹.

The advent of two-dimensional electronic spectroscopy in the last decade has provided access to unprecedented observations of the sub-picosecond excited state dynamics in photosynthetic complexes². By mapping out cross-correlations between excitation and emission events, several experimental groups have reported coherence beating lasting several hundred femtoseconds – a time scale well beyond that expected for electronic dephasing in these noisy, disordered systems. This has generated a widespread scientific debate as well as further research effort on the quantum mechanical picture that can explain such results. One of the ultimate goals of this latest work is to put forward design principles that allow quantum mechanical enhancement of energy transfer processes, thereby linking directly with a wider scientific endeavour of creating a new generation of robust quantum-enhanced technologies.

There is mounting evidence that vibronic coupling and the associated quantum mechanical exchange of energy between excitonic and vibrational degrees of freedom may be at the heart of the counter-intuitive long-lived coherences probed in experiments³. Within this hypothesis, intramolecular vibrations influence excited state dynamics through the formation of delocalized joint quantum

states of electronic and vibrational degrees of freedom⁴. Vibronic coupling is known to have a significant effect on the energy level structure and hence the steady state spectra of molecular aggregates⁵, but its influence on dynamics is a relatively unexplored area. In this issue, Dean *et al.* show that light-harvesting antennae from cryptophyte algae are excellent prototype systems to investigate both the dynamical signatures of these vibronic effects and the enhancement they can provide for excitation transfer⁶.

A previous theoretical description of electronic dynamics in cryptophyte antennae put forward the important role of vibronic coupling involving localised quasi-coherent vibrations with frequencies near-resonant with excitonic energy gaps. This work considered the complex phycoerythrin 545 (structurally similar to the one considered by Dean *et al.*) and concluded that such resonant vibrational modes have a dual role by promoting faster and wider spatial distribution of excitations spanning chromophores that are well separated in space and energy⁷. It has also been predicted that vibrational frequencies larger than the thermal energy scale lead to intermolecular vibronic states exhibiting quantum features with no classical analogue⁴. Nevertheless, a systematic experimental investigation of these issues has been lacking.

Dean *et al.* address this problem by experimentally investigating the vibronic enhancement of energy transfer between spatially separated chromophores in the light-harvesting protein phycocyanin 645 (PC645) from the cryptophyte algae *Chroomonas mesostigmatica* (see Fig. 1). PC645 is unique to cryptophyte algae and operates in addition to chlorophyll-containing complexes also found in higher plants and cyanobacteria. This complex allows the algae to utilize more of the solar spectrum by absorbing in the blue and green. Furthermore, it down converts the excess energy to interface with the chlorophyll-containing complexes, where further energy transfer and conversion steps take place. In contrast to previous studies⁸, the authors focus on the primary energy funnel in PC645 that involves transfer from the central dimer of DBV molecules to peripheral PCB molecules which are a few nanometres apart. This large separation means the electronic coupling ($\sim 38\text{cm}^{-1}$) is much smaller than the energy gap ($\sim 1500\text{cm}^{-1}$) and may initially lead to the expectation that the excitation transfer rate is dominated by the spectral overlap of donor and acceptor line shapes, without the need to take into account any delocalization effects, as described by Förster theory. This hypothesis is contested by the low temperature broadband tran-

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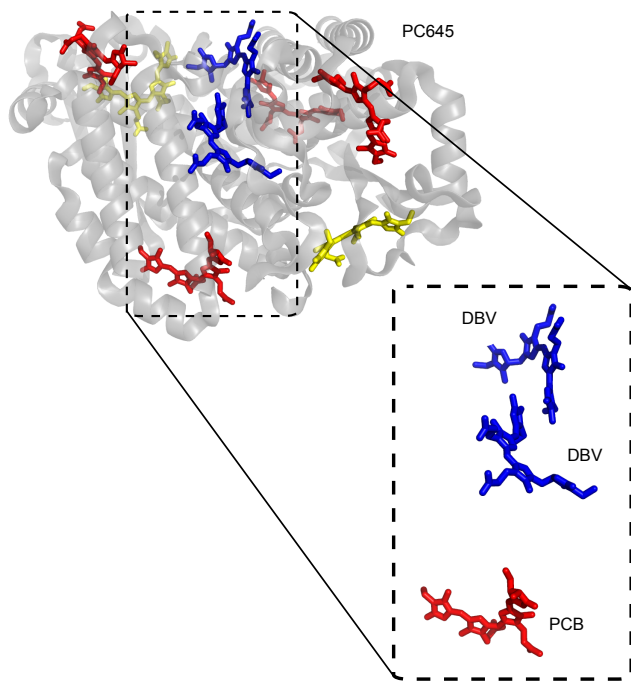


FIG. 1. **Cryophyte light-harvesting complex phyco-cyanin 645.** The protein structure (grey) and arrangement of bilin molecules DBV (blue), MBV (yellow) and PCB (red) is shown. The central DBV dimer and one of the peripheral PCB chromophores are shown close up to illustrate the primary energy funnel. The largest distance between these chromophores is about 3 nm.

sient absorption and the 2D spectroscopy carried out by the authors and which give evidence of a significantly increased rate of transfer between these chromophores in comparison to the predictions of Förster theory. The authors rationalize their observations with an insightful theoretical model in which localised quantized vibrations, arising from the C=N or C=C stretching modes of donor and acceptor and having frequency similar to the electronic DVB-PCB energy gap, provide additional quantum mechanical transfer pathways. In their approximate description, intermolecular vibronic coupling leads to a transfer rate that depends on an effective electronic coupling weighted by the quantum mechanical overlap of vibronic transitions of donor emission and acceptor absorption. Their systematic experimental analysis and accompanying theoretical discussion lends even more weight to the argument that intermolecular vibronic coupling is *the* design principle which enhances energy transfer in cryptophyte algae light-harvesting complexes.

The findings of Dean *et al.* rest on the rigorous analysis of 2D coherence maps which highlight the regions of the spectra that oscillate in a certain frequency window. 2D spectra essentially correlate excitation and third order emission frequencies and allow coherences between particular states to be time-resolved. Concentrating on the frequency of a vibration near-resonant with the DBV-PCB energy gap, the coherence map indi-

cates the existence of long-lived coherence between these chromophores. The estimated dephasing time is roughly 350fs, much longer than the estimated electronic dephasing time at the same temperature (~ 27 fs). Given the dramatic separation in energy and the weak electronic coupling, rationalizing these observations as resulting from electronic coherence alone would be unfounded. A detailed comparison of the coherence amplitudes for different pulse excitations allows the authors to conclude the origin of such oscillations must arise from joint electronic-vibrational quantum states. The main signature being that vibrational transitions of PCB excited states have a larger amplitude than in the ground state. By considering the collective electronic-vibrational quantum states of the donor and acceptor i.e. inter-molecular vibronic states, the authors are able to predict the correct amplitudes of signals in both rephasing and non-rephasing spectra. In order to further understand the physical mechanism and significance behind this observation of vibronic coherence, Dean *et al.* present a simple model that goes beyond Förster theory to quantify the enhancement in the transfer rate. They adapt Jortner-Bixon theory for electron transfer in the presence of an intramolecular vibration for application to energy transfer. The theory accounts for the quantum-mechanical overlap of Frank-Condon transitions associated with a local quantized vibration, while maintaining a second order perturbation with respect to the electronic coupling. The approach also introduces an adiabaticity parameter that gives insight into the competing effects between quantum mechanical overlap and vibrational reorganization, allowing a rough estimation on when vibronic corrections will be needed. An increase in the rate of energy transfer of up to 3.5 times is predicted relative to Förster theory. At ambient temperatures and once disorder is taken into account, the improvement is estimated to be around 10%. This prediction is in line with theoretical work indicating that quantum electronic-vibrational interactions can enhance a figure of merit in the scenario of a quantum heat engine with parameters of PC645⁹.

The theoretical analysis by Dean *et al.* considers only the effect of a single vibrational frequency while all other environmental effects are ignored. Incorporating a wider range of quantized vibrations may make the predicted enhancements more robust to disorder. The insights presented also rely largely on the quasi-local character of the intermolecular vibronic states. This therefore encourages a careful investigation of the overall advantages of vibronic coupling when exciton states with large delocalizations are also involved and the quasi-local picture breaks down. Indeed, a systematic investigation is needed before generalizing these findings to all light-harvesting antennae or reactions centres, where coherence beating has also been observed. While 2D optical spectroscopy has shown to be a powerful technique for unveiling details of ultrafast excited state dynamics, the congested nature of these spectra hinders unambiguous signatures of excited state coherences. Furthermore, the ensemble nature of

the measurement also means a certain amount of information is washed out. Complementary experimental efforts to probe coherence - whether at the ensemble or the single-molecule level¹⁰ - are therefore much needed.

REFERENCES

- ¹Fassioli, F., Dinshaw, R., Arpin, P. C., and Scholes, G. D. *Journal of the Royal Society* **11**(92), 20130901 (2014).
- ²Schlau-Cohen, G. S., Dawlaty, J. M., and Fleming, G. R. *IEEE Journal of Selected Topics in Quantum Electronics* **18**(1), 283–295 jan (2012).
- ³Tiwari, V., Peters, W., and Jonas, D. *Proc. Nat. Acad. Sci. USA* **110**(4), 1203–1208 (2013).
- ⁴O’Reilly, E. J. and Olaya-Castro, A. *Nature Communications* **5**, 3012 (2014).
- ⁵Spano, F. C. *Accounts of Chemical Research* **43**(3), 429–439 (2009).
- ⁶Dean, J., Mirkovic, T., Toa, Z., Oblinsky, D., and Scholes, G. *Chem* (2016).
- ⁷Kolli, A., O’Reilly, E. J., Scholes, G. D., and Olaya-Castro, A. *The Journal of Chemical Physics* **137**(17), 174109 nov (2012).
- ⁸Novelli, F., Nazir, A., Richards, G., Roozbeh, A., Wilk, K., Curmi, P., and Davis, J. *The Journal of Physical Chemistry Letters* **6**(22), 4573–4580 (2015).
- ⁹Killoran, N., Huelga, S. F., and Plenio, M. B. *Journal of Chemical Physics* **143**(15) (2015).
- ¹⁰Weigel, A., Sebesta, A., and Kukura, P. *Journal of Physical Chemistry Letters* **6**(20), 4032–4037 (2015).