Coherent Dynamics in Light-Harvesting Complexes with Two-Colour Spectroscopy

G. H. Richards\textsuperscript{1}, K. E. Wilk\textsuperscript{2}, P. G. Curmi\textsuperscript{2}, H. M. Quiney\textsuperscript{3} and J. A. Davis\textsuperscript{1}

1. Swinburne University of Technology, Melbourne, Australia
2. University of New South Wales, Sydney, Australia
3. The University of Melbourne, Melbourne, Australia

**LIGHT-HARVESTING COMPLEXES**

*Introduction*

In photosynthetic organisms light from the sun is absorbed by Light-Harvesting Complexes (LHCs). Light-harvesting complexes contain chromophores, optically active molecules, held in place in a protein matrix\textsuperscript{1}. Excitations on the chromophores are transferred to a reaction centre (where charge separation takes place and energy can be stored) on the timescale of femtoseconds to picoseconds. Recent work suggests that light-lived quantum coherence can exist between excited states of the chromophores in both the Fenna-Matthews-Ohlon complex (FMO)\textsuperscript{2,3} and Phycocyanin-645 (PC-645)\textsuperscript{4}. These coherences persist on the timescale of energy transfer processes.

- In the experiment two pulses of different colour, separated by a delay \(\tau\) (called the coherence time), interact with the system, preparing it in a coherent superposition of excited states.
- A third pulse interacts with the system after a delay \(T\) (called the waiting time) generating a four-wave mixing signal \(k_3\), as long as the superposition remains coherent.
- The presence of coherent coupling will be indicated by any extended signal for values of \(T\) beyond the pulse overlap region.

**Problem**

Previous work which has identified coherences has relied on 2D spectroscopy using broadband pulses to excite the LHC\textsuperscript{2,3}. The disadvantage of this technique is that in these complex systems there are multiple coherence and population pathways, which are simultaneously excited by the broad bandwidth pulse. This leads to a congested 2D spectrum where pathways are overlapped. Details of individual coherent interactions in the system are difficult or impossible to isolate.

The energy of the first two pulses are tuned to the DBV\textsuperscript{+} and MBV states\textsuperscript{4} of PC-645. The bandwidth of these pulses is approximately 17meV or 15% of the energy separation between the pulses, eliminating the contribution of population pathways to the signal.

**Solution**

- In order to isolate a single coherence pathway we use narrowband pulses to excite the system. Two Optical Parametric Amplifiers (OPAs) are used to generate two spectrally separate pulses.
- These are tuned to be overlapped with two states in PC-645, between which a long-lived coherence was previously identified by 2D spectroscopy\textsuperscript{4}.
- This technique allows us to follow the dynamics of the individual coherence and its interactions with other states, in the absence of other signals.

**RESULTS - LONG-LIVED COHERENT OSCILLATIONS AND THEIR ORIGIN**

**Origin of the oscillations in the \(k_3\) signal**

- The oscillations are quantum beats arising from coherent excitation of multiple states by either of the first two laser pulses.
- The beating component at 22meV may arise from coherent excitation of two states from within the spectrum of a single laser pulse.
- To create beating at 40meV and 74meV, outside the laser spectrum, another state must be coherently excited by some other mechanism.
- In order to excite this additional state and for energy to be conserved the pulse must be absorbed in combination with the emission or absorption of a phonon, as shown in Fig. 1. This suggests the excited states are strongly coupled to phonon modes\textsuperscript{5}.
- Previous work\textsuperscript{6} has identified a state at 2.11eV attributed to DBV\textsuperscript{+}. The energy difference between this state and the states directly excited by the laser pulses are in close agreement with the energy differences identified by the quantum beating.
- Coherent excitation of the DBV\textsuperscript{+} could occur by phonon assisted absorption of the laser pulses or by coherence transfer following direct excitation of the DBV\textsuperscript{+} and/or MBV states.
- To attempt to differentiate these mechanisms we isolate the 40meV and 74meV beat components in the spectral domain and Fourier transform back to the time domain. We are looking for a delayed rise in the signal of the individual beat components in (c) and (d), which is indicative of coherent transfer.

**CONCLUSIONS**

- We have isolated a single coherence pathway in the absence of other excitations.
- We measure the dephasing rate of the coherence as a function of temperature, which suggests that the observed dephasing is primarily due to decoherence caused by phonon interactions.
- We have provided evidence for the strong coupling of excited states to phonon modes which can lead to coherent coupling between non-resonant states in the PC-645 complex.
- We provide evidence that the non-resonant DBV\textsuperscript{+} state is coherently excited. However there are still open questions regarding the nature of the excited states involved and the precise mechanism by which the intermediate state is excited.
- The extension of this technique to the other transitions across the absorption spectrum, in combination with the dependence on polarization and temperature, will provide more information on the nature of the coupling and energy transfer in this light-harvesting complex.

**REFERENCES**

1. B. R. Blankenship, Molecular Mechanisms of Photosynthesis

---

**LIGHT-HARVESTING COMPLEXES**

*Problem*

The final interaction at 2.066eV is non-resonant and produces a spectrally separated signal detected directly by a CCD attached to a spectrometer.

This final interaction is analogous to a coherent Raman signal except that the interaction may also be with an electronic coherence\textsuperscript{5}.

**Solution**

- The final interaction at 2.066eV is non-resonant and produces a spectrally separated signal detected directly by a CCD attached to a spectrometer.
- This final interaction is analogous to a coherent Raman signal except that the interaction may also be with an electronic coherence\textsuperscript{5}.

**RESULTS - DEPHASING**

**Dephasing** figure

- We have isolated a single coherence pathway in the absence of other excitations.
- We measure the dephasing rate of the coherence as a function of temperature, which suggests that the observed dephasing is primarily due to decoherence caused by phonon interactions.
- We have provided evidence for the strong coupling of excited states to phonon modes which can lead to coherent coupling between non-resonant states in the PC-645 complex.
- We provide evidence that the non-resonant DBV\textsuperscript{+} state is coherently excited. However there are still open questions regarding the nature of the excited states involved and the precise mechanism by which the intermediate state is excited.
- The extension of this technique to the other transitions across the absorption spectrum, in combination with the dependence on polarization and temperature, will provide more information on the nature of the coupling and energy transfer in this light-harvesting complex.

**REFERENCES**

1. B. R. Blankenship, Molecular Mechanisms of Photosynthesis