Studying Energy Transfer Dynamics in Light Harvesting Complex II using 2D Electronic-Vibrational Spectroscopy

Nicholas H.C. Lewis[1,2,3]*, Thomas A.A. Oliver[4], Matteo Ballottari[5], Natalie L. Gruenke[1,2,3], Roberto Bassi[5], and Graham R. Fleming[1,2,3]

[1]Department of Chemistry, University of California, Berkeley, California 94720, USA
[2]Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
[3]Kavli Energy Nanoscience Institute at Berkeley, Berkeley, California 94720, USA
[4]School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, United Kingdom
[5]Dipartimento di Biotecnologie, Facoltà di Scienze, Università di Verona, Strada Le Grazie, I-37134 Verona, Italia

Excitation energy transfer dynamics in the photosynthetic protein LHCII from spinach, are studied using 2D electronic-vibrational spectroscopy. We show how energy transfer from Chl *b* to Chl *a* and can be directly observed in LHCII using this multidimensional technique, revealing previously unobserved steps in the excitation transfer pathway.

Light harvesting complex II (LHCII) is the major peripheral antenna complex for photosystem II in plants. A thorough understanding of the excitation dynamics in LHCII is critical for complete model of photosynthetic light harvesting. The energetic structure of this

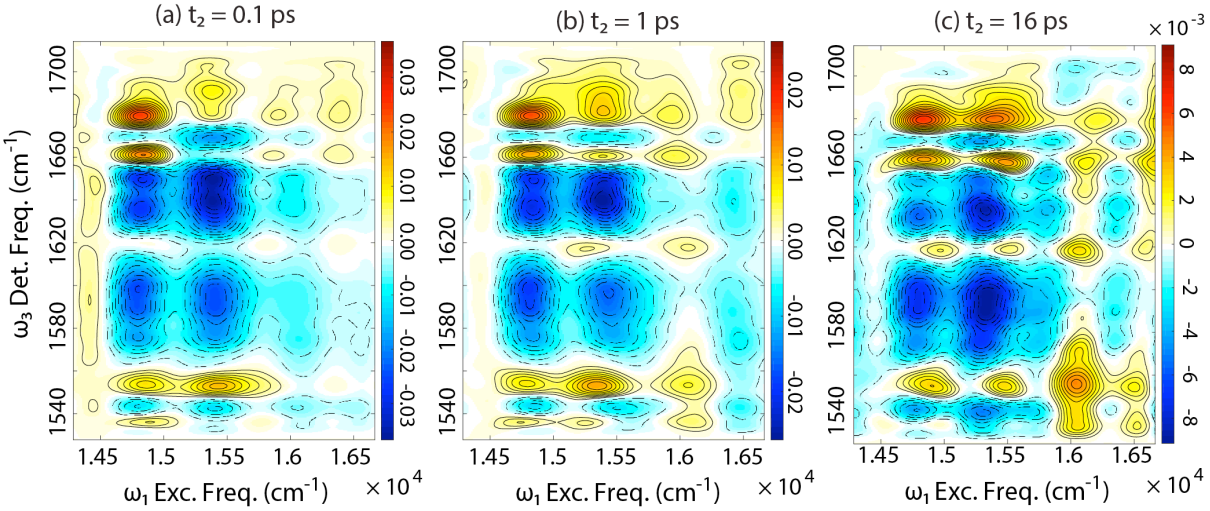

Fig.1 2DEV spectra of LHCII at t_2 = 0.1 ps (a), 1 ps (b) and 16 ps (c). Positive (yellow-red) features indicate ground state vibrational modes, and negative (blue) features indicate excited state modes. Excitation relaxation from Chl *b* to Chl *a* can be observed by monitoring the decay of the Chl *b* vibrational mode at ω_3 = 1700 cm^{-1} excited at ω_1 = 154000 cm^{-1}, and the simultaneous rise of the Chl *a* mode at ω_3 = 1680 cm^{-1}.

system has been studied in detail using electronic spectroscopies,[1-3] but these results can only be linked to energy individual pigments via modeling. Here we present two-dimensional electronic-vibrational (2DEV) spectra of LHCII, shown in Fig.1. This experiment directly relates the electronic states and the spatial location of the excitation within the complex, with chemical specificity. We directly observe the energy transfer from Chl *b* to Chl *a*, revealing that population remains on Chl *b* for far longer than has been previously observed, relaxing on an 8-10 ps timescale. This work provides information about the excitation dynamics with resolution and chemical specificity that has been impossible with standard techniques.

1. Schlau-Cohen, G. S. *et al. J. Phys. Chem. B* **113,** 15352–15363 (2009).
2. Novoderezhkin, V., Marin, A. & van Grondelle, R. *Phys. Chem. Chem. Phys.* **13,** 17093–17103 (2011).
3. Duan, H.-G. *et al. J. Phys. Chem. B* **119,** 12017-12027 (2015).