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Quantum Secrets of Photosynthesis Revealed (2007)

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How photosynthesis achieves a near instantaneous energy transfer from sunlight to chemical energy is a longstanding mystery that may have finally been solved. Researchers have obtained the first direct evidence that long-lived wavelike electronic quantum coherence plays an important part in energy transfer processes during photosynthesis. Computational models guided the design of the experiment and helped interpret the results.

Through photosynthesis, green plants and cyanobacteria are able to transfer sunlight energy to molecular reaction centers for conversion into chemical energy with nearly 100-percent efficiency. Speed is the key — the transfer of the solar energy takes place almost instantaneously so little energy is wasted as heat. How photosynthesis achieves this near instantaneous energy transfer is a longstanding mystery that may have finally been solved.

"We have obtained the first direct evidence that remarkably long-lived wavelike electronic quantum coherence plays an important part in energy transfer processes during photosynthesis," said Graham Fleming, the principal investigator for the study. "This wavelike characteristic can explain the extreme efficiency of the energy transfer because it enables the system to simultaneously sample all the potential energy pathways and choose the most efficient one."

In a paper in the April 12, 2007 issue of the journal Nature, Fleming and his collaborators report the detection of "quantum beating" signals, coherent electronic oscillations in both donor and acceptor molecules, generated by light-induced energy excitations, like the ripples formed when stones are tossed into a pond. Electronic spectroscopy measurements made on a femtosecond (millionths of a billionth of a second) time-scale showed the oscillations meeting and interfering constructively, forming wavelike motions of energy (superposition states) that can explore all potential energy pathways simultaneously and reversibly, meaning they can retreat from wrong pathways with no penalty.

This finding contradicts the classical description of the photosynthetic energy transfer process as one in which excitation energy hops from light-capturing pigment molecules to reaction center molecules step-by-step down the molecular energy ladder.

Fleming and his research group have developed a technique called two-dimensional electronic spectroscopy that enables them to follow the flow of light-induced excitation energy through molecular complexes with femtosecond temporal resolution.

"To observe the quantum beats, 2D spectra were taken at 33 population times, ranging from 0 to 660 femtoseconds," said researcher Greg Engel. "In these spectra, the lowest-energy exciton gives rise to a diagonal peak near 825 nanometers that clearly oscillates (Figure 1). The associated cross-peak amplitude also appears to oscillate. Surprisingly, this quantum beating lasted the entire 660 femtoseconds."

"Computational modeling and simulation at NERSC played a critical role in this research," Fleming said. "Nobody has ever done experiments like this before, so simulations are essential to tell us what the information content of the measurement actually is. I often say to students, it's normal for theory to come in after you've done an experiment, but in our case, the model actually guides the design of the experiment. It tells us what to look for, how to measure it, and how to know what we're looking at."

Yuan-Chung Cheng explained further: "At first we didn't understand why the signal oscillates. To figure that out, we had to run a simulation on a smaller model, which clearly showed that the oscillations correlate with the quantum coherence in the system. It actually represents the energy transfer back and forth in those molecules. So when we figured that out, we could then carry out more large-scale simulations."

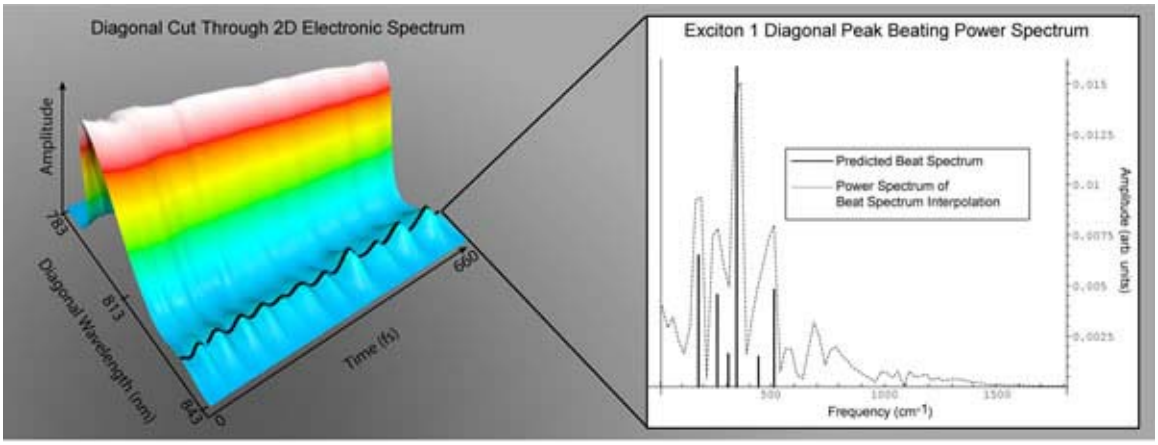

Figure 1. Two-dimensional electronic spectroscopy enables scientists to follow the flow of light-induced excitation energy through molecular complexes with femtosecond temporal resolution. In this 2D electronic spectrum, the amplitude of the quantum beating signal for exciton 1 is plotted against population time. The black line covers the exciton 1 peak amplitude. The experimental data's agreement with the computational simulation is shown on the right.

"It's not just a single system that we have to simulate," Cheng continued, "because in those protein systems there is an intrinsic static disorder, so each individual protein complex is slightly different from the others."

"So we have to repeat the calculation thousands of times to get the averaged behavior of the real set of molecules," Fleming pointed out.

Elizabeth Read added, "Once we have a decent model of what this protein is doing, that enables us to estimate what the frequencies of oscillation will be, and then that tells us how many time points we need to measure in order to be able to observe the quantum coherence, and so it all goes into the design of the experiments. Without these models we would have no basis for doing that."

This kind of modeling requires the capacity of a massively parallel computer. Calculating a 2D spectrum for just one set of initial conditions can take several hours because of the large number of molecules and states involved. The results from thousands of independent calculations with different initial parameters must be averaged, requiring up to 20,000 processor-hours for a complete 2D spectrum.

In addition to the 2D spectrum modeling, the Fleming group also performs quantum dynamics simulations to elucidate the energy transfer pathways inside the network of photosynthetic pigment-protein complexes, and to study the effects of coherence transfer on the energy transfer dynamics. These simulations can take up to 1000 processor-hours per job, depending on the number of molecules being modeled. The researchers' goal is to understand the "design rules" that enable the extremely efficient energy transfer in photosynthesis.

One of the next steps for the group will be to look at the effects of temperature changes on the photosynthetic energy transfer process. They will also be looking at broader bandwidths of energy using different colors of light pulses to map out everything that is going on, not just energy transfer. And they plan to begin studying light-harvesting complex 2 (LHC2), which is the most abundant pigment-protein complex in green plants.

The ultimate goal is to gain a much better understanding of how Nature not only transfers energy from one molecular system to another, but is also able to convert it into useful forms. If we can learn enough to emulate this process, we might be able to create artificial versions of photosynthesis that would help us effectively tap into the sun as a clean, efficient, sustainable, and carbon-neutral source of energy.

Publications:

G. S. Engel1, T. R. Calhoun, E. L. Read, T.-K. Ahn, T. Mančal1, Y.-C. Cheng, R. E. Blankenship, and G. R. Fleming, "Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems," Nature **446**, 782 (2007).

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