PERSPECTIVES: PHOTOSYNTHESIS

Coherent Excitation in the Antenna Complex

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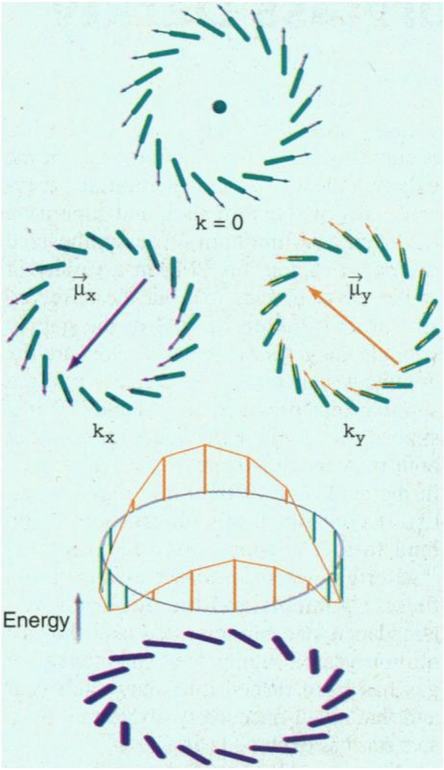
Photosynthesis, the process on which nearly all life on Earth depends for food, relies on a tiny molecular factory called the reaction center that transforms light into chemical energy. The reaction center can perform this transformation at a much higher rate than its intrinsic absorption would allow, particularly under low light conditions, because so-called antenna complexes harvest and funnel light energy into the central machinery. Antenna complexes such as the bacterial LH2 protein complex investigated by van Oijen *et al.* (page 400 of this issue) (*1*) are thus critical components of photosynthetic systems (*2*).

The structure of LH2 has recently been determined by x-ray diffraction (*3*). Besides carotenoids that absorb blue light (at around 470 nm), the complex also contains a loose ring of nine bacteriochlorophyll a (BChl a) molecules that absorb light at 800 nm and a second concentric ring of 18 closely stacked BChl a molecules that absorb at 850 nm. The energy of photons absorbed by the carotenoids or the B800 ring is transferred downhill to the B850 system. Each LH2 assembly contains tens of chromophores, and thus it collects and concentrates light very efficiently.

But how can this energy be transferred further, from the LH2 antenna complex to the LH1 system that surrounds the reaction center? Molecular diffusion is too slow, and trapping of the excitation far from the LH1 complex must be avoided. The natural system has found an elegant solution to this problem: exciton transport. If near-resonant molecules are arranged so that they interact strongly, excitations can travel from molecule to molecule. Such exciton transport between resonant sites can be incoherent or coherent (*4*). The difference between them is easily grasped with the simple picture of two coupled pendula, one of which is excited initially. If the pendula can only interact through occasional hits, they exchange vibrational energy without definite phase relation. If, on the other hand, the two pendula are bound by a spring, they exchange energy periodically (*5*). In their steady vibration modes, the pendula oscillate either in phase or out of phase. This is coherent coupling. For the exciton coupling in LH2 to be coherent, the π electron of each BChl a molecule must oscillate with a given phase shift with respect to its neighbors. However, the degree of coherence of the B850 excitons is difficult to infer from structural data or even from time-resolved optical experiments on ensembles (*2*, *6*).



Schematic structure of the B850 ring. This ring consists of 18 BChl a molecules and forms one part of the LH2 antenna complex. In the state $k = 0$ of the defect-free ring, all molecules oscillate in phase, so that the total dipole moment of this state is zero (**top**). The states k_x and k_y are degenerate (that is, they have the same energy), carry all the oscillator strength, and have perpendicular polarizations (**middle**). A structural distortion may induce correlated energy shifts in the individual BChl a molecules and may break the degeneracy. For example, the energy pattern shown at the bottom of the figure would shift the k_x exciton's transition energy downward and that of the k_y exciton upward.

By isolating a single LH2 in the focus of a microscope at liquid helium temperature, van Oijen *et al.* (*1*) have now unraveled its fluorescence excitation spectrum at a spectacular resolution. However, the qualitative difference between the spectra of the B800 and B850 systems is even more striking. Whereas the several narrow lines of the B800 ring point to long-lived states localized on single, weakly coupled molecules in the nine-membered ring, the small number of bands of the strongly coupled B850 ring are intense and broad. They suggest collective modes and fast relaxation to lower lying states, two hallmarks of exciton coupling (*7*). The B850 spectrum can be understood at once from a naïve exciton picture (see the figure), with coherent exciton states delocalized over the perfect ring. The dipole moment of an optical transition is a vector that characterizes the amplitude and direction of the electronic movement upon absorption. For the lowest, $k = 0$ exciton state, it is essentially nil (blue arrows in the figure), whereas those of the two orthogonal states k_x and k_y are strong and perpendicular (purple and yellow arrows) (*8*). The perpendicular polarizations of the two main experimental bands (*1*) strongly support their attribution to these exciton states k_x and k_y, split by a perturbation of the ninefold symmetry of the ring. Further support for exciton coherence is provided by the narrow absorption line found at the red edge of the excitation spectrum and attributed to the lowest state, $k = 0$ (*1*).

Random shifts of the resonance frequencies of individual BChl a molecules cannot explain the large energy splittings that are observed in these spectra between states that should be degenerate in the perfect ring. A global distortion of the antenna complex could either cause correlated site energy shifts such as those drawn schematically in the figure, which would result in a positive (negative) shift for state k_y (k_x), or modulate exchange interactions, as in the model of van Oijen *et al.* (*1*).

These results illustrate the power of single-molecule methods in biophysics and show that optical spectra can complement x-ray structures by providing information on subtle structural distortions. The evidence for exciton coherence in the LH2 complex, at least at low temperature, is very important for understanding photosynthesis and raises the question of the biological function of coherence. A coherent addition of electric fields can strongly enhance energy transfer by the Förster mechanism (*9*), and as Sundström *et al.*

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pointed out (*2*), this might be crucial for the energy transfer from LH1 to the reaction center. A more efficient energy transfer allows a larger distance between the LH1 ring and the two strongly interacting chlorophyll-like molecules in the reaction center that trap the excitation; the separation serves to prevent charge transfer back to LH1 after ionization.

Finally, the characterization of an individual LH2 complex is a theorist's dream come true in molecular spectroscopy. With the structure known, detailed comparisons between theory (*10*) and experiment become possible. As one of the first examples of single-molecule spectroscopy in strongly interacting systems, van Oijen *et al.*'s study bridges the gap between studies of narrow zero-phonon lines (10^{-3} cm^{-1}) at low temperatures and those of broad bands (100 cm^{-1}) of dye molecules at room temperature (*11*). The spectral resolution of 1 cm^{-1} in (*1*) is compatible with the use of short (picosecond) laser pulses and could lead to the fascinating prospect of time-resolved investigations of single molecules.

References and Notes

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8. The lowest excited state is $k = 0$ for the negative dipole-dipole interaction of the B850 ring. The states k_x and k_y are linear combinations of the circularly polarized states $k = 1$ and $k = -1$, which present a phase rotation by 360° when going around the ring. They are the only dipole-allowed states in the perfect ring.
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PERSPECTIVES: COSMOCHEMISTRY

Through an Hourglass Darkly

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How can we learn about about the early history of our solar system and the recent history of our galaxy? Astronomers and cosmochemists use a suite of radioactive isotopes as chronometers to study these important scientific questions. By comparing the measured abundance of an accumulated daughter nuclide and the inferred initial abundance of the parent radioactive species, these isotopes can serve as hourglasses that determine the time since the initial radioactive abundance was set. Among the hourglasses used, ^{26}Al [with a half-life ($\tau_{1/2}$) of 7.15×10^5 years] has proven to be one of the most valuable but also one of the most puzzling. Astronomers have used this isotope to great advantage in recent years to understand star formation in our galaxy. But cosmochemists are still struggling to determine how ^{26}Al can help them understand the conditions under which the solar system formed.

Aluminum-26 was the first radioactive isotope detected from interstellar space. In 1979, the High Energy Astronomical Observatory satellite observed the 1.809-MeV gamma-ray that is emitted during ^{26}Al's decay (*1*). Since then, experiments aboard the Compton Gamma-Ray Observatory have established from the observed gamma-ray flux that a steady-state abundance of about 3 solar masses ($M_\odot$) exists in our galaxy's interstellar medium today (*2*). These observations show that element formation has occurred over the past million years in the galaxy and provide information about recent rates of star formation and supernova occurrence. Aluminum-26 is synthesized by proton capture on ^{25}Mg in a variety of stellar environments (*3*), but the observed spatial distribution of ^{26}Al in the galaxy strongly suggests that massive stars are the dominant source (*4*). The recently inferred simultaneous presence of ^{26}Al and ^{44}Ti in a supernova remnant in Vela suggests that both radioactive isotopes were synthesized in the explosion of the same massive star (*5*). If confirmed, this observation would lend further support to the idea that the ^{26}Al originates from massive stars. From these arguments and the observed ^{26}Al abundance, one can infer that over the past million years roughly 5 $M_\odot$ of interstellar gas has been turned into stars each year and that about once every 30 years a massive star has exploded (*6*).

Aluminum-26 may also provide insights into the early history of our solar system. Millimeter-sized calcium- and aluminum-rich inclusions (CAIs) in certain meteorites are solids formed extremely early in the solar nebula and are among the most primitive objects in the solar system. Many contain excess ^{26}Mg compared with the average concentration in the solar system. Magnesium-26 is the daughter of ^{26}Al, and the excess ^{26}Mg correlates with the concentration of aluminum in these CAIs. From these observations, it can be inferred that ^{26}Al was present at an abundance of $^{26}\mathrm{Al}/^{27}\mathrm{Al} \approx 5 \times 10^{-5}$, the so-called "canonical" level (*7*), when the object condensed. Two outstanding puzzles remain regarding ^{26}Al in the early solar system: Why was its concentration so high? And was it homogeneously distributed? How well ^{26}Al can be used as an hourglass for studying the early solar system's history depends on the answers to these two questions.

From the inferred $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ value in the CAIs, one would expect an abundance of about 30 $M_\odot$ in the current steady-state interstellar medium, about 10 times that actually observed from the gamma-ray measurements. Furthermore, ^{26}Al-rich supernova debris are typically not directly injected into molecular cloud cores where stars form but rather into hotter phases of the interstellar medium where it must mix into cloud cores on 10^8-year time scales. When this is accounted for, the meteorites contain about four orders of magnitude too much ^{26}Al compared with expectations for a steady-state interstellar medium (*8*). This implies that the live ^{26}Al in the early solar system was not a residue of ongoing, continuous galactic nucleotide synthesis but rather was produced shortly before CAI formation. A massive star may have exploded just before the sun's birth (perhaps triggering the collapse of the solar cloud) and injected the ^{26}Al-rich debris into the solar nebula (*9*). Alternatively, energetic particles from the ambient molecular cloud (*10*) or from the protosun itself (*11*) could have synthesized ^{26}Al locally in the solar nebula. Both possibilities receive ongoing scrutiny. However, the recently detected excesses of ^{41}K in samples from the early solar system and their correlation with calcium content suggest that the even shorter lived ^{41}Ca ($\tau_{1/2} = 1.0 \times 10^5$ years) was also alive in the early system (*12*). The correlation of live ^{41}Ca with live ^{26}Al in CAIs tends to favor the massive-star injection scenario (*13*).

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