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ON A POSSIBILITY OF SELF-ORGANIZATION IN
PHOTOSYNTHETIC LIGHT HARVESTING ANTENNAE

Karl K. REBANE. FOTOSONTEESIKS VALGUST KOGUVA ANTENNI ENESEORGANISEERIMISE
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Карл К. РЕБАНЕ. ОБ ОДНОЙ ВОЗМОЖНОСТИ САМООРГАНИЗАЦИИ АНТЕННЫ, СОБИРАЮ-
ЩЕЙ СВЕТ ДЛЯ ФОТОСИНТЕЗА

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One of the problems of photosynthesis is what the mechanisms and kinetics of energy transfer are. Quite a number of models has been proposed. As far as I know, all of them are the models for lifeless world, like e.g. models for describing the luminescence of crystals. The destination of energy transfer in photosynthesis is to build and support living matter. It seems quite interesting to consider also some possibilities of self-organization, which is a very characteristic feature of life. It is not excluded that self-organization starts already at such an early stage of life as energy transfer in light harvesting antenna.

Two extreme situations may be considered for the energy transfer. The first is random migration. The second is strictly correlated structure and firmly directed energy transfer. The second should be faster in energy transport, and consequently should have a higher yield. Further, in the second case the antenna may be larger, because a well-channelled and fast transfer takes the excitation energy to the photosynthetic unit over long distances before it is emitted as light or otherwise lost. But a system of the second kind may be both in construction and in energy transfer vulnerable to rather small defects and perturbations. A system of the first kind — the one with randomness in its build-up — can be more stable against flaws of structure and various happenings. But the first system may be slower in energy transfer, which means more losses of energy via emission of light or nonradiative processes. On the other hand, if the randomness provides the ability for self-organization, the performance can be considerably improved in the transfer process itself. Nature starts with rather random systems which in the course of action «learn» to become more effective. Self-organization may also provide an increase of stability.

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In this note I would like to call attention to a rather simple probability of self organization of the molecular system of the light-harvesting antenna. Such a mechanism of "self-education" could be photochemical transformations of the molecules in the course of energy transfer analogous to photoburning of spectral holes, but in addition to some spectral selectivity, high site selectivity should take place. This mechanism can eliminate traps for excitation energy on its route of random migration to the reaction center.

We suppose that the spectral bands of absorption and luminescence are bell-shaped, continuous and lacking sharp line structure. It is not difficult to take into account sharp lines, e.g. zero-phonon lines present usually in low (liquid helium) temperature spectra of impurity molecules [1]. The mechanisms proposed below will also work and their influence should be even stronger when spectra comprise sharp lines.

The energy of electronic excitation acquired by an antenna molecule via absorption of a photon starts migrating in a system of more or less similar molecules. The energy transfer from one molecule to the next one is fast as compared to the migrating excited electronic state's lifetime on the body of antenna molecules. But on the other hand, time spent on one particular molecule is sufficient for some vibrational relaxation to take place. We suppose that the transfer mechanism is a resonant one, e.g. the Förster-Galanin mechanism, but complete vibrational relaxation to the thermal equilibrium is not obligatory. Presence of coherent or hot transfer processes [2] does not change the basic picture, provided the relaxation is not too small.

Somewhere in the middle of the antenna sits a reaction center, a certain structure of a pair of chlorophyll molecules with its specific surrounding, which, as soon as it has caught the excitation, performs the next step of photosynthesis — utilizes the excitation energy to separate the elementary electrical charges.

Antenna comprises a body of chemically identical molecules bound in complexes. Physical conditions are slightly different and the spectra of absorption and luminescence of the body of antenna molecules are inhomogeneous. The energy of the purely electronic transition and vibronic transitions varies from molecule to molecule. As the energy transfer is vibronic (electron-vibrational), the Franck-Condon principle governs the probabilities, and the overlapping of the luminescence spectrum (including the hot luminescence part) of the donor with the absorption spectrum of the acceptor is the measure of the number of the populated vibronic levels of the donors from which the energy can be resonantly given to acceptors, and also of the efficiency of transfer. Further, as far as some vibrational relaxation is present, the luminescence of the donor is shifted to longer wavelengths as compared to the acceptor's absorption, even if their electronic energies are equal. This shift increases with the amount of relaxed vibrational energy. The maximum of the overlapping between the luminescence of the donor, and the absorption of the acceptor is shifted to the anti-Stokes region of the donor's absorption. If the relaxed energy is large in comparison with the sum of the absorption and the luminescence bandwidths, the overlapping becomes smaller and the transfer is strongly restricted. Overlapping increases when the purely electronic transition energy of the acceptor (e.g. because of inhomogeneity) is smaller than that of the donor and the transfer goes faster. In the presence of a notable inhomogeneous shift the excitation is preferentially given to that particular acceptor in the donor's surrounding whose absorption band has the largest shift to red.

The probability of the opposite transition, from the now excited molecule back to the initial donor, is, in addition to the Stokes shift,

suppressed by the inhomogeneous shift of the previous acceptor's luminescence to red. Transfer obtains the character of a process directed along a line of molecules arranged in the order of the most rapidly decreasing electron energies. If the absorption spectrum of the reaction center lies sufficiently towards the longer wavelengths and therefore has a good overlapping with the luminescence of the antenna molecules, the last step of the transfer to the center is fast. Because of large overlapping, it may be even so efficient that the energy could be directly transferred to the center from a distance of many molecules. The area of antenna may be divided into an inner and an outer circles. As soon as excitation appears in the first one, it will be directly and fast transferred to the center. In the outer circle created to enlarge the harvesting area, the energy has first to migrate out of it and enter the inner circle. The migration may be time and energy consuming. Self-organization — improving efficiency of the outer circle — is welcome. Energy migrating along a line in the inhomogeneous body of antenna molecules in the outer circle may be trapped: its path may end at a molecule whose red shift is so strong that all the acceptors available at a distance are out of resonance (no overlapping), and migration stops. Here is the point where self-organization may step in: as further transfer is strongly restricted, the excitation stays at this molecule for a very long time as compared to the normal transfer times. During this long waiting time the probability accumulates for some photochemical reaction in the molecule or its surroundings and it can bring along changes of the spectra of the trap molecule. This may well detune the resonance that brought excitation to this particular trap molecule. For example, it is the case when photo-product of the trap molecule has its absorption band considerably shifted to shorter wavelengths and the overlapping with the luminescence of potential donors drops well below limits of effective competition with the other potential acceptors in the donors vicinity. If the first trapped excitation does not perform photochemistry, the following ones will. A trap molecule which was a normal acceptor and could not work as a donor, is converted into a very bad acceptor and becomes an outsider of the migration.

Probability to undergo photochemistry is approximately proportional to time that excitation spends at this particular molecule. It means that a trap molecule on a busy road of migration will be burned out sooner than a trap in a quiet street. We can see here a self-organizing mechanism clearing away the traps from the pathway of the electronic excitations through the inhomogeneous body of antenna molecules in the outer circle towards the inner circle and towards the reaction center.

What happens under strong illumination? Shouldn't then all the antenna molecules be turned into outsiders? Indeed, the reaction center cannot accept the next excitation before transformation of the previous one is completed. A number of excitations may be rejected, and they have to continue migrating and initiating photochemistry outside the reaction center. Fast degradation may be avoided if the rejected excitations remain migrating in the inner circle. The electronic energies of the molecules in the vicinity of the reaction center, i.e. in the inner circle, may have quite strong red shifts caused by nearby presence of the center: Excitations will be captured in the inner circle. Further we assume that molecules close to the center are more stable to photochemistry or that photochemistry works and causes many changes, but in the inner circle it does not matter. The second assumption seems reasonable. The red shifts determined by position (not far from the reaction center) are large enough to preserve overlapping and ability to accept energy from the outer antenna area even after the photochemically induced shifts have

taken place. As soon as reaction center becomes free, the waiting in migration excitation will be accepted by it. Energy levels of reaction center are still more red shifted and one-step fast transfer is possible.

What should be observed if this mechanism would really work? Firstly, the efficiency of a newly-born antenna should increase during some period of time after it was exposed to illumination. After a longer working time efficiency may gradually fade away, because the integrated time of being excited becomes long even for the normally transferring molecules. Secondly, the antenna molecules must show photochemical changes. Experiments confirm the presence of sensibility to persistent spectral hole burning in systems of chlorophyll molecules in low temperature solids [3] and in photosynthetic units [4]. Thirdly, the product of trap removal — phototransferred antenna molecules — should be present, their number increasing initially with the extent of "learning", afterwards — with the amount of molecules worn out in long service.

Up to now, according to the model, the photochemical changes were irreversible. Self-organization would also work if reverse or almost reverse reactions were present. Of course, these reactions should not be fast. A proper amount of reversibility makes the model even more flexible — the antenna would last longer. An almost reverse reaction may change an outsider into a normal acceptor and normal donor. Further, if a considerable part of molecules is converted to outsiders, they may form a new hierarchy of energy transferring molecules and establish new effective energy routes. Reversible mechanisms may work creating (and reversing) photoproducts, which are quite difficult to distinguish from the educts. The main question seems to be whether the Stokes and inhomogeneous shifts are large enough to really influence the transfer rates at photosynthetic temperatures via the overlapping of spectra. Even when they are too small to guarantee complete trapping, the effect of longer stay at bad donors remains, and they will preferably be "burned out".

The presented above is a rather speculative idea. Nevertheless, it might be not useless if it would stimulate to look for features of self-organization in photosynthesis. New possibilities for speculation on kinetic equations and, in particular, for computer simulations, are also being opened.

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